U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-301 384

Atmospheric Reaction Products of Organic Compounds

SRI International, Menlo Park, CA

Prepared for

Environmental Protection Agency, Washington, DC Office of Toxic Substances

Jun 79

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-560/12-79-001	2.
3. RECIPIENT'S ACCESSION NO. PB301384	
4. TITLE AND SUBTITLE Atmospheric Reaction Products of Organic Compounds Final Report	5. REPORT DATE June 1979 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Dale G. Hendry and Richard A. Kenley	8. PERFORMING ORGANIZATION REPORT NO. PYU-8395
9. PERFORMING ORGANIZATION NAME AND ADDRESS Office of Chemical Control Office of Toxic Substances U.S. Environmental Protection Agency Washington, D.C. 20460	10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-01-5123
12. SPONSORING AGENCY NAME AND ADDRESS Office of Chemical Control Office of Toxic Substances U.S. Environmental Protection Agency Washington, D.C. 20460	13. TYPE OF REPORT AND PERIOD COVERED Final Technical Report 14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

A procedure has been developed to predict the products from reaction of compounds in the atmosphere. The procedure is designed to be used in unreasonable-risk evaluations that include assessing new chemicals for persistence and exposure in the environment.

In this procedure, the relative importance of the three dominant reaction pathways--photolysis, reaction with OH radical, and reaction with ozone--are first determined for each compound. Then the products from each pathway that play a major role for that compound are estimated using the techniques outlined in the methods.

The methods are applicable to a wide variety of compounds; however, as the structure of the compounds differ from the structures on which the procedures were based, the conclusions become tentative. It is believed, however, that this will be a minor fraction of the cases to which it is applied.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Unlimited distribution through National Technical Information Service Springfield, Va. 22151	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES 90
	20. SECURITY CLASS *(This page)*	22. PRICE A05-A01

EPA Form 2220-1 (9-73)

EPA-560/12-79-001
June 1979

ATMOSPHERIC REACTION PRODUCTS OF ORGANIC COMPOUNDS

by

D. G. Hendry and R. A. Kenley

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

Contract No. 68-01-5123

Project Officer

Stuart Z. Cohen
Office of Chemical Control
Washington, D. C. 20460

OFFICE OF CHEMICAL CONTROL
OFFICE OF TOXIC SUBSTANCES
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D. C. 20460

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

DISCLAIMER

This report has been reviewed by the Office of Toxic Substances, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

A general procedure has been developed to predict the products resulting from reaction of various compounds in the atmosphere. The procedure is designed to be used in unreasonable-risk evaluations that include assessing new chemicals for persistence and exposure in the environment.

In this procedure, the relative importance of the three dominant reaction pathways--photolysis, reaction with OH radical, and reaction with ozone--are first determined for each compound. Then the products from each major pathway are estimated using the techniques that have been developed.

The methods are applicable to a wide variety of compounds; however in cases where the structure of the compounds differ in type from the structures on which the procedures were based, the conclusions may be less certain. Although it is not possible to anticipate the new structures to which the procedure will be applied, only a minor fraction of the cases are expected to fall into this latter category.

CONTENTS

	Page
ABSTRACT	iii
FIGURES	vii
TABLES	viii
1. INTRODUCTION	1
2. CONCLUSIONS AND RECOMMENDATIONS	3
3. BACKGROUND	4
General Considerations	4
Importance of OH and O_3 Reactions	5
Basis for Prediction of Reaction Products	13
4. ESTIMATING RATES OF ATMOSPHERIC REACTIONS	14
Hydroxyl Radical Reactions	14
Ozone Reactions	21
Photochemical Transformations	22
5. PRODUCTS FROM REACTIONS OF OH	30
Products Resulting from Hydrogen Abstraction	31
Atmospheric Reaction of Peroxy Radicals	31
Chemistry of Alkoxy Radicals	32
Bimolecular Reactions	32
Unimolecular Reactions	33
Products Resulting from Addition of OH to C=C Double Bonds	40
Products from Addition to Aromatic Compounds	42
6. PRODUCTS FROM REACTIONS OF OZONE	49
7. PHOTOCHEMICAL REACTION PRODUCTS	53
General	53
Limitations	53
Photochemical Reactions	57
Carbonyl Compounds	57
Olefins	62
Nitrites, Nitrates, Nitro and Nitroso Compounds	63
Halides	65
Procedures	65
8. PREDICTIVE SCHEME	69
Step 1. Estimation of Rates of Environmental Processes	69
Estimation of the Rate Constant of Reaction with OH (k_{OH}) and τ_{OH}	69
Estimation of the Rate Constant for Reaction with Ozone (k_{O_3}) and τ_{O_3}	70
Estimation of the Rate Constant for Photolysis ($\bar{k}_p$) and τ_p	71
Step 2. Estimation of Products from OH Reactions	71

C-H Bond Reactions 71
C=C Bond Reactions 72
Aromatic Ring Reactions 72
Relative Concentration of Products 72
Step 3. Estimation of Products from O_3 Reactions . . . 73
Step 4. Estimation of Products from Photolysis 73

INDEX 74
REFERENCES 76

FIGURES

Number		Page
1	Correlation of Rate Constants for Addition of OH to Substituted Benzenes with Substituent Constants $\Sigma\sigma_\rho$	20
2	Prediction of Products for 1,1-Dichloroethane	39
3	Prediction of Products for 3-Chloro-4-Hydroxy-*cis*-butenoic Acid Methyl Ester	43
4	Prediction of Products for 3-Chloro-Ethylbenzene	49

TABLES

Number		Page
1	Apparent First-Order Rate Constants for Reactions of Atmospheric Oxidants with Propene, n-Butane, and Toluene	6
2	Rate Constants and Environmental Half-Lives for Reactions of Hydroxyl Radicals near 300°K	7
3	Rate Constants and Environmental Half-Lives for Reactions of Ozone at 300°K	10
4	Abstraction Rate Constants (k_H) for Reactions of OH with Generalized Groups and Values of Induction Factors (α_H and β_H) .	17
5	Addition Rate Constants (k_E) for Reaction of OH with Carbon-Carbon Bond and Values of Induction Factors (α_A)	18
6	Addition Rate Constants (k_A) for Reaction of OH with Aromatic Rings and Values of Induction Factors (α_A)	19
7	Rate Constants for Reaction of Ozone with Generalized Structures	23
8	J_λ' Values at 10°N Latitude	25
9	J_λ' Values at 30°N Latitude	26
10	J_λ' Values at 50°N Latitude	27
11	Examples of Hand Computation of Photochemical Rate Constants . .	28
12	Estimated Rate Constants for Reactions of Primary, Secondary, and Tertiary Alkoxy Radicals	35
13	Estimated Rate Constants for Reaction of Methoxy Substituted Alkoxy Radicals	37
14	Selected Values of Hammett σ_p	46
15	Products from Reaction of Ozone and Alkenes under Atmospheric Conditions	51

Number

Page

16 Approximate Absorption Regions for Organic Molecules 54

17 Bond-Dissociation Energies for Some Organic Molecules R'-R" . . 56

18 Products of Photochemical Reactions 67

SECTION 1

INTRODUCTION

Both chemical and physical processes compete in determining the fate of chemicals in the atmosphere. The more reactive compounds react rapidly within the boundary layer immediately adjacent to the surface of the earth where they enter the troposphere. Less reactive compounds will be distributed by diffusion and turbulent mixing into the remainder of the troposphere where reaction will occur over a longer period of time. Compounds that are stable in the troposphere and not removed by physical processes will gradually diffuse into the stratosphere where additional loss mechanisms exist--the more important being reaction with $O(^1D)$ and photolysis in the 150-300 nm region of the solar spectrum above the ozone layer.

To understand the effects of industrial chemicals on the environment, it is important to be able to anticipate not only what the rates of the possible processes are for each chemical but also what the products will be from these processes. This is especially important because the effect of introducing a chemical into the troposphere on the environment is not limited to the chemical, physical, and biological interactions of that chemical but also involves the effect of products derived from various reactions of that chemical.

Under EPA Contract No. 68-03-2227, SRI International has prepared procedures to assess the rates of dominate atmospheric processes for chemicals (Hendry et al., 1979). These procedures involve two levels: first, a screening level where rates are approximated based on the generalized chemical structures in the literature data, and second, an experimental level where rate constants for processes that are potentially critical are determined. Using the procedures in the first level, we can readily approximate the rate of individual processes for many chemicals without further experimental study and thereby predict the lifetimes of the chemicals in the environment.

The objective of this study is to review concepts and data on product formation from tropospheric reactions and to develop procedures for predicting transformation products of new chemical substances in the atmosphere. The methods should be suitable for use in unreasonable-risk evaluations that include assessing new chemicals for persistence and exposure in the environment.

The general approach is to identify structure-reactivity relationships that correlate existing rates of reaction and that will be useful in predicting rates of reaction of new structures. The success of this approach depends not only on the reliability of the correlations between structure and reactivity but also on the application of new structures to that correlation. To the extent that a new compound introduces a new structural variation, which will

often be the case for a new industrial chemical, it is difficult to know what reliability a correlation will have, if it can be applied at all, for such a compound. Therefore, these correlations cannot be totally successful in predicting the reaction rates and products of new structures. However, they will be very helpful in many cases, especially when the structure is consistent with those structures where a correlation has been demonstrated.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

A predictive procedure has been set forth to anticipate the products resulting from the reaction of compounds in the atmosphere. The methods should find application to a wide variety of compounds and be suitable as part of the persistence and exposure assessment of new chemicals. The ultimate goal has been to use structure reactivity relationships to assist in the predictions; however, the cases where such relationships have been applied to gas-phase reactions of importance to atmospheric reactions are very limited, and in general, the study of the effect of structure, as has been investigated in the solution phase, has not been explored.

An investigation of methods of correlating atmospheric reactions of OH and O_3 should yield useful results. The success in correlating the rate constants for addition of OH to aromatic rings with σ-type substituent constants and the rate constants of cleavage of alkoxy radicals with the heats of reaction indicate these methods should be extended. There are two levels of this general problem that deserve further consideration. First, using the current data base extend our initial effort to investigate types of structural parameters that best correlate the data. For example, do solution phase parameters of the Hammett type correlate OH and O_3 reactions adequately, or do parameters like electron affinity or ionization potential apply more satisfactorily? The second level would be to enlarge the experimental data base on which to test various methods of correlation. The types of structures that we have OH and O_3 rate constant data for are limited and determination of rate constants for a wider range of structures would be very helpful.

Finally, our knowledge of atmospheric gas-phase photo reactions is very limited. One major problem centers around our anticipating whether or not oxygen quenches the photo-excited states of the compounds of interest and thereby prevent product formation. In many cases, this factor can mean the difference between a rapid reaction due to photolysis or no reaction at all. A detailed review of the literature of oxygen quenching would be helpful in determining what generalizations regarding quenching are possible.

SECTION 3

BACKGROUND

GENERAL CONSIDERATIONS

The detailed atmospheric chemistry by which compounds containing carbon- and hydrogen are largely converted to CO_2 and H_2O and by which organic nitrogen and sulfur are converted to nitrates and sulfates is quite complex (Leighton, 1961; Demerjian et al., 1974; Pitts and Finlayson, 1975; Baldwin et al., 1977; Hendry et al., 1978; Carter et al., 1978). We have spent considerable effort studying these processes, and our understanding is reasonably good, although semi-quentitative. Currently we are developing chemical mechanisms that describe the chemistry of individual hydrocarbons to simulate the chemistry occurring in smog chambers. These simulations are reasonably effective in predicting the smog chamber results.

Our understanding of atmospheric chemistry is sufficient to allow identification of the critical chemical processes that will affect the lifetime of chemicals in the atmosphere. These processes involve oxidation reactions and photochemical transformations. These two basic processes are defined as follows.

Oxidation reactions involve interaction of a compound in its electronic ground state with a reactive species such as oxygen, ozone, O atom, or OH radical. In this case, the rate determining step is the bimolecular reaction of compound and reactive species

$$\text{Rate of Oxidation} = k_{OX}[OX][C]$$

where k_{OX} is the rate constant for the process, [OX] is the concentration of reactive species, and [C] is the concentration of chemical.

Photochemical transformations are those reactions wherein the compound absorbs solar energy directly to form an electronically excited intermediate that undergoes further reactions by either first-order or second-order processes. In all cases the rate determining step is the absorption of solar energy and follows the relation

$$\text{Rate of Phototransformation} = \phi I_a/h$$

where I_a is the light absorbed (in photons cm^{-2} s^{-1}), h is the depth (in cm) over which the light is absorbed, and ϕ, quantum yield, is the fraction of

excited species that reacts.

IMPORTANCE OF OH AND O_3 REACTIONS

Except for some compounds that photolyze rapidly, the most important reactions of organic compounds in the atmosphere are with OH radical and ozone. Table 1 summarizes approximate daytime concentrations of these species along with several other oxidants also believed to be present in the atmosphere. Included in the table are rate constants for reaction of these oxidants with propene, n-butane, and toluene, which are common atmospheric pollutants. The product of the rate constant and the concentration of oxidant is the apparent first-order rate constant (k'_{OX}) for that process.

$$\text{Rate} = k_{OX}[OX][C] = k'_{OX}[C]$$

Clearly, in the case for propene the reaction with OH is most important, while the reaction with O_3 is second most important. Together, OH and O_3 account for more than 99% of the reaction; ground state oxygen atom ($O(^3P)$ accounts for only 0.1% of the reaction. For both n-butane and toluene, OH alone accounts for greater than 99% of the reaction. These conclusions obviously are dependent on the concentrations that are assigned for each oxidant. However, the concentrations of OH and O_3 are not expected to vary significantly from the values in the table.

In some cases a compound might have unusually high reactivity to one of the other oxidants, although this should be the exception. One important case is the oxidation of NO by HOO• (or ROO•). The reaction

$$HOO\bullet + NO \longrightarrow HO\bullet + NO_2$$

is the major route by which NO is oxidized in the atmosphere. The reaction competes favorably with the reaction with ozone. However, to our knowledge, there are no cases involving organic compounds where reactions with oxidants other than OH and O_3 are important.

Thus, to estimate the lifetime of chemicals in the atmosphere as determined by oxidation processes, we need to determine only the rate constants for reactions with OH and O_3. The rate constants for reaction of numerous compounds with OH and O_3 are summarized in Tables 2 and 3.

The lifetime(τ) for reaction of substrate (S) with an oxidant is defined

$$\tau = \frac{[S]}{k_{OX}[OX][S]} = 1/k_{OX}[OX]$$

where k_{OX} is the bimolecular rate constant and [OX] is the approximate concentration of the reactive species. The time to deplete one-half of the chemical is referred to as the half-life ($t_{\frac{1}{2}}$) and is defined

TABLE 1. APPARENT FIRST-ORDER RATE CONSTANTS FOR REACTIONS OF ATMOSPHERIC OXIDANTS WITH PROPENE, n-BUTANE, AND TOLUENE[a]

Oxidant	Concentration[b] (molec cc^{-1})	Propene		n-Butane		Toluene	
		k_{OX}, cc molec^{-1} s^{-1}	k_{OX}[OX], s^{-1}	k_{OX}, cc molec^{-1} s^{-1}	k_{OX}[OX], s^{-1}	k_{OX}, cc molec^{-1} s^{-1}	k_{OX}[OX], s^{-1}
OH	2×10^{6}	2.5×10^{-11}	5×10^{-5}	2.7×10^{-12}	5×10^{-6}	6.4×10^{-12}	1×10^{-5}
O_3	1×10^{12}	1.0×10^{-17}	1×10^{-5}	~ 0	~ 0	~ 0	~ 0
$O(^3P)$	3×10^{4}	3.5×10^{-12}	1×10^{-7}	5.2×10^{-9}	2×10^{-4}	7.5×10^{-14}	2×10^{-9}
$O(^1D)$	2×10^{-1}	$\sim 1 \times 10^{-14}$	2×10^{-12}	$\sim 1 \times 10^{-11}$	2×10^{-12}	$\sim 1 \times 10^{-11}$	2×10^{-12}
$HO_2\cdot$ ($RO_2\cdot$)	1×10^{10}	$< 2 \times 10^{-18}$	$< 2 \times 10^{-8}$	~ 0	~ 0	$\sim 1 \times 10^{-18}$	1×10^{-8}
$O_2(^1\Delta_2)$	1×10^{9}	$\leq 1.7 \times 10^{-20}$	$\leq 2 \times 10^{-11}$	~ 0	~ 0	~ 0	~ 0
NO_3	2×10^{8}	5.3×10^{-13}	1×10^{-4}	~ 0	~ 0	~ 0	~ 0

[a] Rate constants from references shown below; concentrations are estimated based on smog chamber stimulation data from Hendry (1978); rate constants were taken from Hampson and Garvin (1978), Hendry and Mabey (1978), Demerjian, Kerr, and Calvert (1974); Japar and Niki (1975).

[b] To convert to ppm multiply by 4.1×10^{-14}; to convert to M, multiply by 1.7×10^{-21}.

TABLE 2. RATE CONSTANTS AND ENVIRONMENTAL HALF-LIVES FOR REACTIONS OF HYDROXYL RADICALS NEAR 300°K[a]

Compound	$10^{13}\ k_{OH}$, $cm^3\ molec^{-1}\ s^{-1}$	$t_{\frac{1}{2}}$, days[b]
Alkanes		
Methane	0.0079	1,000
Ethane	0.29	28
Propane	2.2	3.6
Methyl	2.2	3.6
Dimethyl	0.81	9.9
n-Butane	2.7	3.0
Methyl	3.3	2.4
2,3-Dimethyl	5.1	1.6
2,2,3-Trimethyl	3.8	2.1
2,2,3,3-Tetramethyl	1.1	7.3
n-Pentane	6.5	1.2
2-Methyl	5.3	1.5
3-Methyl	7.1	1.1
2,2,4-Trimethyl	3.8	2.1
n-Hexane	6.0	1.3
n-Octane	8.5	0.9
Cycloalkanes		
c-Butane	1.2	6.7
c-Pentane	6.1	1.3
c-Hexane	7.0	1.1
Haloalkanes		
Methane		
Fluoro-	0.016	500
Difluoro-	0.0078	1,030
Trifluoro-	0.0002	40,000
Tetrafluoro-	< 0.0004	> 20,000
Chloro-	0.04	200
Dichloro-	0.14	57
Trichloro-	0.11	73
Tetrachloro-	< 0.0004	> 20,000
Bromo	0.04	200
Ethane		
Chloro	0.39	20
1,1-Dichloro	0.26	31
1,2-Dichloro	0.22	36
1,1,1-Trichloro	0.015	530
1,1,1-Trifluoro-2-chloro	0.010	800
1,1,1-Trifluoro-2,2-dichloro	0.028	280
1,1,1,2-Tetrafluoro-2-chloro	0.012	670
1,2-Dibromo	0.25	32
Alkanone		
Butanone	3.3	2.4
2-Methylpentanone	14.9	0.54
2,6-Dimehtylheptanone	24.9	0.32
Alkanols		
Methanol	0.95	8.4
Ethanol	3.0	2.7
Propanol	3.8	2.1
2-Propanol	7.1	1.1
Butanol	6.8	1.2
4-Methyl-2-pentanol	7.1	1.1
O,N,S Substituted alkanes		
Methyl ether	3.5	2.3
Ethyl ether	9.3	0.86
n-Propyl ether	17.3	0.46

TABLE 2 (continued)

Compound	10^{12} k_{OH}, cm^3 $molec^{-1}$ s^{-1}	$t_{\frac{1}{2}}$, days[b]
O,N,S Substituted alkanes		
Tetrahydrofuran	14.6	0.55
1-Propylacetate	4.5	1.8
2-Butylacetate	5.6	1.4
Methylamine	21.9	0.37
Methyl sulfide	33.9	0.24
Formaldehyde	15	0.53
Acetaldehyde	16	0.50
Propionaldehyde	21	0.38
Benzaldehyde	13	0.61
Alkenes		
Ethene	7.9	1.5 0.85
Propene	24.8	0.5
Methyl-	50.6	0.2
1-Butene	35.4	0.3
2-Methyl	58.1	0.2
3,3-Dimethyl	28.2	0.4
2-Butene		
cis-	53.6	0.2
trans-	69.9	0.2
2-Methyl	79.7	0.1
2,3-Dimethyl	153	0.1
1-Pentene	29.9	0.4
cis-2-Pentene	64.8	0.2
1-Hexene	31.5	0.4
1-Heptene	36.5	0.3
Cycloalkenes		
c-Cyclohexene	71.4	0.2
1-Methyl	96.3	0.1
Haloalkenes		
Ethene		
Fluoro	5.6	1.4
1,1-Difluoro	2.0	4.0
Chloro	6.6	1.2
Trichloro	2.0	4.0
Tetrachloro	0.17	47
Chlorotrifluoro	7.0	1.1
Bromo	6.8	1.2
O-Substituted alkene		
Methoxy	33.5	0.24
Alkadienes		
Propadiene	4.5	2.6
1,3-Butadiene	77	0.1
2-Methyl	78	0.1
Terpenes		
p-Menthane	6.6	1.2
α-Pinene	25.7	0.31
β-Pinene	21.6	0.37
3-Carene	28.2	0.28
Carvomenthane	41.5	0.19
β-Phellandrene	38.2	0.21
d-Limonene	48.1	0.17
Dihydromyrcene	59.7	0.13
Myrcene	74.7	0.11
cis-Ocimene	105	0.076

TABLE 2 (concluded)

Compound	10^{12} k_{OH}, cm^3 $molec^{-1}$ s^{-1}	$t_{1/2}$, days[b]
Alkynes		
Ethyne	0.16	50
Methyl	0.95	8.4
Aralkanes		
Benzene	1.4	5.7
Methyl	5.9	1.3
1,2-Dimethyl	13	0.62
1,3-Trimethyl	20	0.40
1,4-Trimethyl	10	0.80
1,2,3-Trimethyl	24.7	0.32
1,2,4-Trimethyl	33.2	0.24
1,3,5-Trimethyl	49.3	0.16
Ethyl	7.5	1.1
1,2-Ethylmethyl	13.6	0.59
1,3-Ethylmethyl	19.4	0.41
1,4-Ethylmethyl	12.9	0.62
propyl	6.0	1.3
2-propyl	7.8	1.0
1,4-methylpropyl-2-	15.2	0.53
hexafluoro	0.22	36
propylpentafluoro	3.0	2.7
Substituted Aralkanes		
Methoxybenzene	19.6	0.41
o-Cresol	34.0	0.24

[a] Compiled from data and references in Pitts et al., 1977, and Hampson and Garvin, 1978.

[b] Environmental half-lives in 24-hour days, assuming an OH concentration equal to 1×10^6 radicals cm^{-3}.

TABLE 3. RATE CONSTANTS AND ENVIRONMENTAL HALF-LIVES FOR REACTIONS OF OZONE AT 300°K

Compound	10^{18} k_{O_3}, cm^3 $molec^{-1}$ s^{-1}	Reference	$t_{\frac{1}{2}}$, days
Alkanes			
Methane	1.4 (-6)	a	5.73 (6)
Ethane	1.2 (-6)	b	6.68 (5)
Propane	6.8 (-6)	a	1.18 (6)
Methyl	2.0 (-6)	a	3.95 (5)
n-Butane	9.8 (-6)	a	8.18 (6)
Alkenes			
Ethene	1.9	h	4.22
Propene	13	h	0.617
Methyl-	15.1	h	1.30
1-Butene	12.3	h	0.652
2-Butene			
cis-	161	h	0.05
trans-	260	h	0.031
2-Methyl	493	h	0.016
2,3-Dimethyl	1510	h	0.005
1-Pentene	10.7	h	0.75
2-Pentene			
cis-	456	h	0.018
trans-	563	h	0.014
1-Hexene	11.1	h	0.723
1-Heptene	8.14	e	0.99
1-Octene	8.14	e	0.99
1-Decene	1.08	e	7.43
Cyclohexene	169	h	0.047
Conjugated Alkenes			
1,3-Butadiene	8.4	h	0.95
Phenylethene	171.0	i	0.05

TABLE 3 (continued)

Compound	10^{18} k_{O_3}, cm^3 $molec^{-1}$ s^{-1}	Reference	$t_{1/2}$, days
Halogenated Alkenes			
Ethene			
Chloro	1.96	i	4.09
1,1-Dichloro	3.67 (-2)	i	2.19 (2)
1,2-Dichloro			
cis	6.14 (-2)	g	1.31 (2)
trans	3.82 (-1)	g	2.10 (1)
Trichloro	5.98 (-3)	i	1.34 (3)
Tetrachloro	1.66 (-3)	i	4.83 (3)
Tetrafluoro	134	c	.06
Propene			
3-Chloro	18.3	i	.438
Hexafluoro	21.6	c	.37
Terpenes			
α-Pinene	164	d	.05
Alkynes			
Ethyne	7.8 (-2)	j	102.8
Aromatic Hydrocarbons			
Benzene	4.65 (-5)	f	1.72 (5)
Methyl	2.76 (-4)	f	2.91 (4)
1,2-Dimethyl	1.58 (-3)	f	5.09 (3)
1,3-Dimethyl	1.30 (-3)	f	6.19 (3)
1,4-Dimethyl	1.58 (-3)	f	5.09 (3)
1,3,4-Trimethyl	4.65 (-3)	f	1.76 (3)
1,3,5-Trimethyl	6.97 (-3)	f	1.15 (3)
1,2,4,5-Tetramethyl	1.78 (-2)	f	4.51 (2)
Pentamethyl	8.30 (-2)	f	96.6
Hexamethyl	0.407	f	19.71
Ethyl	5.65 (-4)	f	1.42 (4)

TABLE 3 (concluded)

Compound	10^{18} k_{O_3}, cm^3 $molec^{-1}$ s^{-1}	Reference	$t_{1/2}$, days
Aromatic Hydrocarbons			
Benzene (cont.)			
1,3-Diethyl	1.78 (-3)	f	4.51 (3)
1,3,5-Triethyl	5.64 (-3)	f	1.42 (3)
Pentaethyl	1.74 (-2)	f	4.61 (2)
Hexaethyl	5.58 (-3)	f	1.44 (3)
2-Propyl	5.81 (-4)	f	1.38 (4)
t-Butyl	1.15 (-4)	f	6.97 (4)

[a]Schubert and Pease (1956).
[b]Morrissey and Schubert (1963).
[c]Heicklen (1966).
[d]Ripperton and Jeffries (1972).
[e]Cadle and Schadt (1952).
[f]Nakagawa, Andrews, and Keefer (1960).
[g]Blume, Hisatsune, and Heicklen (1976).
[h]Japar, Wu, and Niki (1974).
[i]Williamson and Cvetanovic (1968).
[j]Cadle and Schadt (1953).

$$t_{\frac{1}{2}} = \ln 2/k_{OX}[OX] = \tau \ln 2$$

BASES FOR PREDICTION OF REACTION PRODUCTS

Because photolysis and reactions with OH and ozone are the dominant reactions of organic compounds in the atmosphere, we must be able to predict the products of these reaction. If, from estimates of the rate constants, we can determine that one process dominates the other two, then we know the products from that dominant process will be the atmospheric products. If more than one process is dominant, then the products will reflect the contribution of those reactions. Thus, the reaction of compound C is expressed

$$d[C]/dt = k_{OH}[OH][C] + k_{O_3}[O_3][C] + k_p[C]$$

$$= \{k_{OH}[OH] + k_{O_3}[O_3] + k_p\}[C]$$

The fraction of C reacting during each process and thus the contribution of each process to the products is

$$\%R_x \text{ by OH reaction} = \frac{k_{[OH]}[OH]}{k_{OH}[OH] + k_{O_3}[O_3] + k_p}$$

$$\%R_x \text{ by } O_3 \text{ reaction} = \frac{k_{O_3}[O_3]}{k_{OH}[OH] + k_{O_3}[O_3] + k_p}$$

$$\%R_x \text{ by photolysis} = \frac{k_p}{k_{OH}[OH] + k_{O_3}[O_3] + k_p}$$

Therefore, to determine relative importance of each process we must know the constants [OH] and [O_3]. We previously have shown that the annually averaged ground level concentration of OH is best estimated by 10^6 molecules/cm^3, and the average ozone concentration is best estimated by 10^{12} molecules/cm^3 (Hendry, 1979). Thus, the ability to estimate the constants for the three basic processes is the key to predicting what products are important.

SECTION 4

ESTIMATING RATES OF ATMOSPHERIC REACTION

HYDROXYL RADICAL REACTIONS

From the data in Table 2 it is possible to make several generalizations about OH reactivity that can be useful in estimating the reactivity of compounds. Most alkanes, except methane and ethane, react toward OH with a rate constant of 1 to 10 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}. The reaction with alkanes entails abstraction of hydrogen to form water and an alkyl radical

$$-\overset{|}{\underset{|\beta}{C}}-\overset{|}{\underset{|\alpha}{C}}-H + OH \longrightarrow -\overset{|}{\underset{|\beta}{C}}-\overset{|}{\underset{|\alpha}{C}}\cdot + H_2O$$

Substituents can have many different effects. Single halogen atoms in the α-position activate the carbon-hydrogen bond, but in the β-position they tend to deactivate the bond. Thus, single halogen atoms do not have a large effect on the reactivity of any alkane except methane. Multiple halogens in a molecule generally deactivate the molecule relative to the parent alkane. Thus, 1,1,1-trichloroethane is about 1/20 as reactive as ethane; one-half of the reduction is due to the reduction of the number of available hydrogens, and then the remaining hydrogens are reduced in reactivity by 1/10.

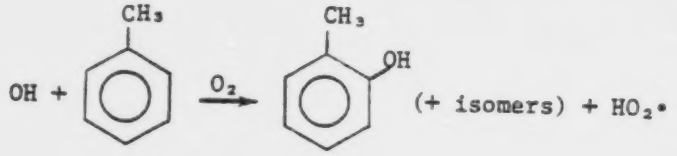
In ketones, alcohols, ethers, and esters, activation occurs relative to the parent hydrocarbon after correction for the number of hydrogens. Amines and sulfide appear to show even larger rate enhancement due to activation of adjacent C-H groups.

The carbon-carbon double bond is much more reactive than the carbon-hydrogen bond and reacts by addition of OH, which generally causes cleavage of the double bond (Niki et al., 1978).

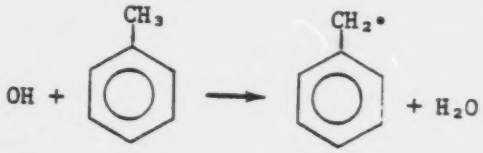
$$\diagdown\!\!\overset{|}{C}\!\!=\!\!\overset{|}{C}\!\!\diagup + OH \longrightarrow HO\overset{|}{C}-\overset{|}{C}\cdot$$

Rate constants for these processes are sensitive to the degree of alkyl substitution on the double bond and vary from 20-200 x 10^{-12}. Consequently, alkenes have a half-life in the environment one-tenth of that for most alkanes. Halogens tend to reduce alkene reactivity somewhat, whereas methoxy has the same effect as an alkyl group. Conjugated dienes have reactivities equal to two double bonds. The reactivities of terpenes are consistent with the similarly substituted alkenes. Alkynes appear to be significantly less reactive than the corresponding alkenes.

Aromatic hydrocarbons have reactivities about the same as alkenes as a result of addition of OH to the ring (Kenley et al., 1978). For examples, 85% of the time, the reaction of toluene with OH adds to the ring giving mainly



Hydrogen abstraction (shown below) occurs only 15% of the time.



It is desirable to be able to estimate rate constants for reaction of various kinds of organic structures with OH. A reasonably reliable predictive scheme can be developed on the basis that the rate constant or total molecular reactivity of a molecule is the sum of rate constants for reactivities of each portion of the molecule, and that little or no effect is exerted on the reactivity of a specific site by a substituent more than two atoms away. Thus, the same group in different molecules is assumed to have the same reactivity. For example, the methyl groups in all alkanes are assumed to have the same reactivity; however, methyl groups in compounds like toluene, acetone, and methyl chloride are assumed to have potentially different reactivities because the second atom from the hydrogen which is abstracted is different.

The chemistry of OH reactions is largely limited to the three kinds of reactions discussed above: abstraction of a hydrogen atom, addition to a carbon-carbon double bond, and addition to an aromtic ring. The rate constant for OH attack is the sum of the rate constant for each of these processes:

$$k_{OH} = k(\text{H-abstraction}) + k(\text{C=C addition}) + k(\text{ring addition})$$

The rate of hydrogen atom abstraction is affected by substitution on the same and adjacent atoms. The total rate constant for abstraction (k_H) may be expressed as the summation of the rate constants for each reactive hydrogen atom as suggested by Greiner (1970)

$$k_H = \sum_{i=1}^{i} n_i \alpha_{Hi} \beta_{Hi} k_{Hi}$$

where k_{Hi} is the reactivity of the ith hydrogen atom and depends on the degree of substitution on the adjacent atom and on whether a vinyl or phenyl group is attached. The terms α_H and β_H account for the effect of substituents other

than hydrogen; α_H is the constant for the substituent in the α-position and β_H is the substituent in the β-position. The term n_i is the number of times the same type of hydrogen group with the same α and β substituents appears in the molecule. Greiner (1970) and Darnall et al. (1978) have applied this type of expression to simple alkane reactivity where α and β = 1. Values of k_H, α_H, and β_H are given in Table 4.

The rate constant for addition to a carbon-carbon double bond (k_E) is expressed by

$$k_E = \sum_{j=1}^{j} \alpha_{E_j} k_{E_j}$$

where k_{E_j} is the reactivity of the jth carbon-carbon double bond and depends on the degree of substitution by carbon, oxygen, nitrogen, or sulfur but not halogen. The α_{E_j} term is unity unless a halogen is immediately attached to the double bond. Values of k_E and α_E are given in Table 5.

Similarly, the rate constant for addition to aromatic rings (k_A) is expressed by

$$k_A = \sum_{\ell=1}^{\ell} \alpha_{A\ell} k_{A\ell}$$

where $k_{A\ell}$ is the reactivity of the ℓth aromatic ring toward OH addition, which depends on the degree of alkyl substitution. The $\alpha_{A\ell}$ is a factor to account for the effect of halogen atoms substituted in the ring. Table 6 summarizes values of k_A and α_A.

In Figure 1 we have plotted the report value of the rate constants for addition to aromatic rings versus the summation of σ_ρ values for the substituent on the benzene ring. Monosubstituted and polysubstituted ring data appear to fall on two separate lines. These expressions can be used to predict k_A for a much wider variety of structures, although it has not been tested for strong electrons with drawing substituents.

Thus the total molecular rate constant (k_{OH}) can be expressed by the sum of these three processes:

$$k_{OH} = \sum_{i=1}^{i} n_i \alpha_{Hi} \beta_{Hi} k_{Hi} + \sum_{j=1}^{j} \alpha_{E_j} k_{E_j} + \sum_{\ell=1}^{\ell} \alpha_{A\ell} k_{A\ell}$$

The reactivities of four representative compounds are tabulated on page 21. Upper and lower limits are given in parentheses following the best estimates. In these examples the uncertainty in the estimated value of k_{OH} is about a factor of 2, the range being one-half the estimate to twice the estimate. Rate constants have been measured for the first two examples and the data are given.

TABLE 4. ABSTRACTION RATE CONSTANTS (k_H) FOR REACTION OF OH WITH GENERALIZED GROUPS AND VALUES OF INDUCTION FACTORS (α_H AND β_H)

Group[a]	10^{12} k_H[b] (per hydrogen)	Substituent, X[c]	α_H[c]	β_H[c]
C_SCX_2-H	0.065 ± 0.013	H	1.0	1.0
$(C_S)_2CX$-H	0.55 ± 0.07	Cl, Br	2.4 ± 0.6	0.4 ± 0.1
$(C_S)_3C$-H	2.9 ± 0.58	F	1.0	0.3 ± 0.1
C_D-H	0.01 ± 0.002	OH	2.0 ± 0.05	1.0
C_DCX_2-H	0.3 ± 0.1	O-alkyl	6.0 ± 2.0	1.0
$(C_S)(C_D)CX$-H	2.5 ± 1.0	$OC(=O)$-	1.0	1.0
$(C_S)_2(C_D)C$-H	4.0 ± 1.5	C-	1.3 ± 0.2	1.0
		N<	100 ± 50	1.0
		S-	200 ± 100	1.0
$-C(=O)-H$	17 ± 4	all cases	1.0	1.0
S-H	2.6 ± 1.3			
C_DO-H	1.7 ± 0.8			

[a] C_S = saturated carbon, -O, -C=O, or S; C_D = unsaturated carbon as in vinyl or phenyl groups; X = H, F, Cl, Br, or other groups listed in third column.

[b] Rate constant expressed as cm^3 $molec^{-1}$ s^{-1}.

[c] See text for application.

TABLE 5. ADDITION RATE CONSTANTS (k_E) FOR REACTION OF OH WITH CARBON-CARBON BOND AND VALUES OF INDUCTION FACTORS (α_E)

Substituent	$10^{12}k$[a] (per double bond)	Substituent α_E[b]
none (ethene)	7.9	
1-alkyl	27 ± 5	H = 1.0
1,1-dialkyl	50 ± 10	F = 0.5 ± 0.3
1,2-dialkyl		Cl,Br = 0.7 ± 0.3
cis	60 ± 12	
trans	70 ± 14	
trialkyl	80 ± 16	
tetraalkyl	150 ± 30	
vinyl or phenyl	80 ± 20	
OMe	33	

[a] Rate constant expressed as cm^3 $molec^{-1}$ s^{-1}.

[b] See text for application.

TABLE 6. ADDITION RATE CONSTANTS (k_A) FOR REACTION OF OH WITH AROMATIC RINGS AND VALUES OF INDUCTION FACTORS (α_A)

Substituent	$10^{12}k$[a]	Substituent[b]	α_A[b]
H	1.4	H	1.0
alkyl	5.0 ± 2	Cl,F,Br	< 1.0
dialkyl	12 ± 4		
1,2,3-trialkyl	10 ± 5		
1,2,4-trialkyl	25 ± 5		
1,3,5-trialkyl	49 ± 5		
methoxy	17 ± 5		
OH plus alkyl	34 ± 10		
-CH (O)	< 1.0		

[a] Rate constant expressed as cm^3 $molec^{-1}$ s^{-1}.

[b] See text for application. Effect of substituent may also be estimated from Figure 1.

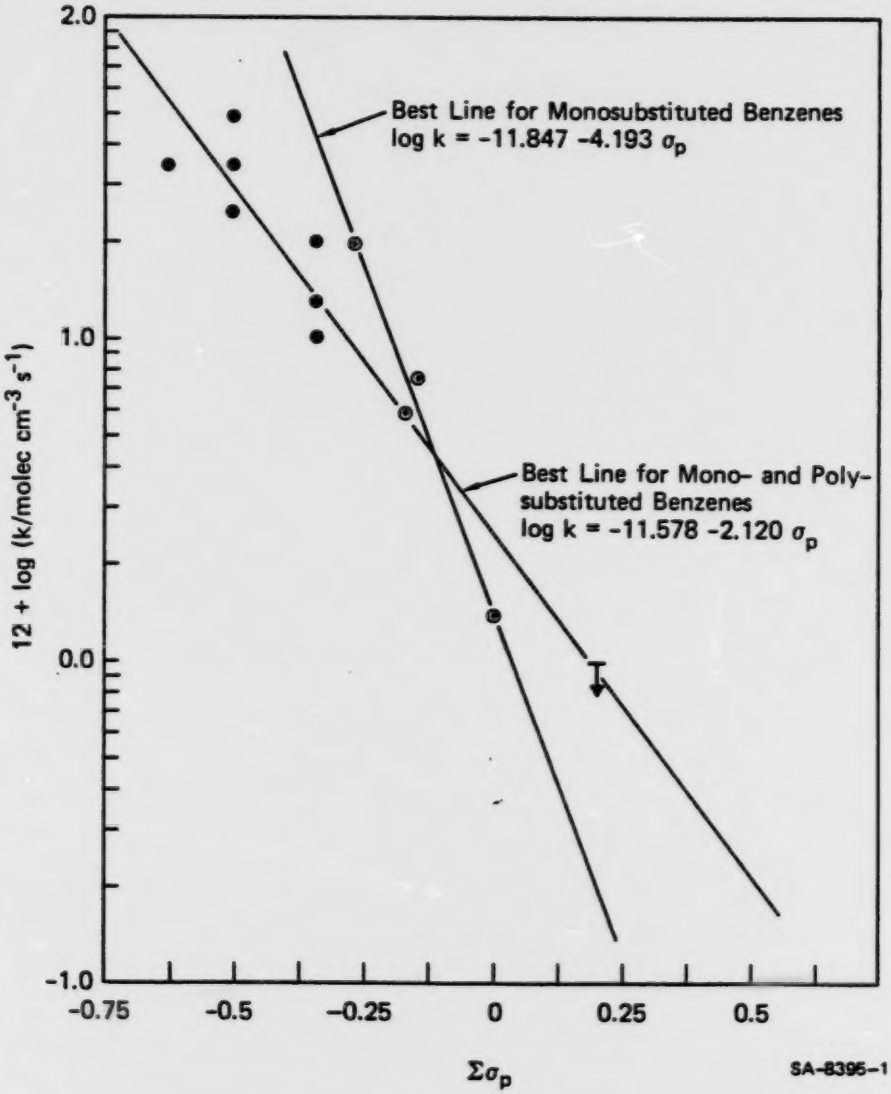


FIGURE 1 CORRELATION OF RATE CONSTANTS FOR ADDITION OF OH TO SUBSTITUTED BENZENES WITH SUM OF SUBSTITUENT CONSTANTS $\Sigma\sigma_p$

1,2-Dichloroethane: $ClCH_2CH_2Cl$

$H_2CClCCl$: $4(0.065 \pm 0.013)(2.4 \pm 0.6)(0.4 \pm 0.1) = 0.25(0.11 - 0.47)$

Measured value (Table 3) = 0.22

1,1-Dichloroethane: Cl_2CHCH_3

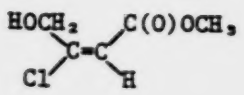
$HCCl_2C$: $(0.065 \pm 0.013)(2.4 \pm 0.6)^2 = 0.37(0.17 - 0.70)$

H_3CCCl_2: $3(0.065 \pm 0.013)(0.4 \pm 0.1)^2 = 0.03(0.015 - 0.06)$

$\Sigma = 0.40(0.17 - 0.72)$

Measured value (Table 3) = 0.26

3-Chloro-4-hydroxy-cis-butenoic acid methyl ester:



cis-C=C: $(60 \pm 12)(0.7 \pm 0.3) = 42(15 - 72)$

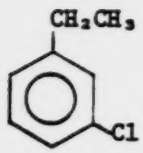
$-CH_2-$: $2(2.5 \pm 1)(2.0 \pm 0.5) = 10(4.4 - 17.6)$

CH_3-: $3(0.55 \pm 0.07) = 1.6(1.4 - 1.9)$

C=C-H: $(0.01 \pm 0.002) = 0.01(0.008 - 0.012)$

$\Sigma = 54\ (21 - 91)$

3-Chloroethylbenzene



ring: 0.6 (Figure 1) = 0.6(0.5 - 0.7)

$-CH_2-$: $2(2.5 \pm 1)$ = 5(3 - 7)

CH_3-: $3(0.065 \pm 0.013)$ = 0.2(0.16 - 0.23)

ring-H: $4(0.01 \pm 0.002)$ = 0.04(0.03 - 0.05)

Σ = 5.84(3.5 - 7.9)

OZONE REACTIONS

The only organics that react with ozone fast enough for the reaction to be environmentally significant are the alkenes and some of the aromatic hydrocarbons. Table 7 summarizes the effect of structure on the rate constants. The substituent increases the reactivity of the carbon-carbon double bond, but the effects are small. Most all alkenes appear to have rate constants in the range of 1.6-22 x 10^{-18} cm^3 $molec^{-1}$ s^{-1}. These rate constants are about 10^7 times larger than those for reaction with OH radical. However, the ratio of the average atmospheric concentrations of ozone to OH is about 10^6 or slightly larger, so that, on the average, reactions of alkenes with ozone are about one-tenth as fast as the reactions with OH. In some cases, because of variations of OH and ozone concentrations in the atmosphere, the ozone reaction could predominate.

The rate constants for reaction of aromatic hydrocarbons with ozone vary over a wide range, from less than 10^{-21} to 10^{-18} cm^{-3} $molec^{-1}$ s^{-1}. Because ozone concentrations range from 0.3-3 x 10^{12} molec cm^{-3}, only under the most favorable conditions can the half-lives be less than a few days, in which case the ozone reactions compete favorably with the OH reactions. However, for most aromatic compounds, ozone reactions are unimportant relative to OH reactions.

PHOTOCHEMICAL TRANSFORMATIONS

The rate of photochemical reaction depends on the absorption of solar energy, which is determined by Beer-Lambert law:

$$I_{o\lambda}/I_\lambda = e^{\sigma_\lambda C\ell}$$

where $I_{o\lambda}$ (in photons cm^{-2} sec^{-1}) is the intensity of incident light at a given wavelength entering a layer of atmosphere, I_λ (also in photons cm^{-2} sec^{-1}) is the intensity of transmitted light, σ_λ is the cross section (in cm^2) at wavelength λ, C is the concentration of chemical (in molecules cm^{-3}), and ℓ is the path length of light. The light absorbed at each wavelength by the chemical ($I_{a\lambda}$) is expressed

$$I_{a\lambda} = I_{o\lambda} - I_\lambda = I_{o\lambda}(1-e^{-\sigma_\lambda C\ell}) \qquad (1)$$

where α_λ is the absorption cross section in cm^2 $molec^{-1}$ at wavelength λ, C is the concentration and ℓ the pathlength. Under atmospheric conditions equation (1) may be simplified

$$I_{a\lambda} = I_{o\lambda}\sigma_\lambda C\ell$$

The rate of photochemical reaction is the light absorbed by the compound in the solar spectrum (I_a) divided by the height (h) of the layer times the quantum efficiency (ϕ).

TABLE 7. RATE CONSTANTS FOR REACTION OF OZONE WITH GENERALIZED STRUCTURES[a]

Structure	$10^{18} k_{O_3,i}$, cm^3 $molec^{-1}$ s^{-1}	$t_{1/2}$, days[b]
Ethenes	1.9	4.2
alkyl	12	0.7
1,1-dialkyl	14	0.6
1,2-dialkyl		
cis-	160	0.06
trans-	260	0.03
trialkyl	500	0.01
tetraalkyl	1500	0.006
Cycloalkenes		
C_5	800	0.01
C_6	170	0.05
Alkadienes		
1,3-butadiene	8.4	1.0
Benzene	0.00005	2×10^3
alkyl	0.003 - 0.0006	2×10^4
dialkyl	0.001 - 0.002	7×10^3
trialkyl	0.006 - 0.008	2×10^3
tetraalkyl	0.02	400
hexaalkyl	0.4	20
hydroxy	1-2	3-7

[a]Data from Table 3.

[b]24-hour days.

$$\text{Rate} = \frac{I_a}{h} = \phi C \Sigma \sigma_\lambda J_\lambda$$

where J_λ is the $I_{o\lambda}$ corrected for zenith angle θ ($\cos \theta = h/\ell$) and is referred to as the actinic flux.

The apparent first-order rate constant (k_p) is thus

$$k_p = \phi \Sigma \sigma_\lambda J_\lambda$$

which is conveniently independent of C and h (concentration and depth of the atmospheric layer). Thus the photochemical reaction rate constant may be calculated from the measured cross section of a compound, J_λ and ϕ. Schere and Demerjian (1977) have published a computer routine to perform this integration over 10-nm wavelength intervals. The routine calculates momentary photochemical rate constants throughout the day for any day of the year at any latitude and longitude. The J_λ values of Peterson (1976) are used in the calculations. Because most compounds require more than one day to photolyze, it is necessary to integrate the output from the Schere and Demerjian routine over time to obtain rates on a day basis.

To facilitate the computation of photochemical rate constants, we have prepared in Tables 8 through 10 day-averaged light intensity values as a function of wavelength at latitudes of 10, 30, and 50°N for the summer and winter solstices and the equinox. In addition, the tables include average rates for spring-summer and fall-winter light intensity values. The light intensity values in the tables refer to J_λ' values and represent the total available actinic light flux in a given wavelength region for a specific day and at a specific latitude. The wavelength ranges in Tables 8 through 10 are divided into 31 intervals over the total range 290-800 nm to maintain reliability of the calculations and yet to allow them to be performed rapidly.

The data in Tables 8 through 10 are multiplied by the average absorption coefficients over the wavelength ranges in the appropriate table with corresponding J_λ' values and summing

$$\bar{k}_p = \Sigma \sigma_\lambda J_\lambda'$$

where $\bar{k}_p = k_p/\phi$ and is an upper limit of k_p; it will equal k_p if $\phi = 1$. The value of k_p corresponds to the latitude and time of year of the J_λ' values used. To demonstrate the hand computation, Table 11 shows calculations of the photolysis rates for benzaldehyde and biacetyl.

Estimating the photo rate imposes a major limitation in estimating the rate constants for the individual processes. The difficulty is caused by the assumption that photo reaction occurs with a unity quantum yield. This assumption gives a maximum rate photo transformation. Although there are several photochemical and photophysical reasons why the quantum yield need not be unity, we will briefly discuss only two of the more important reasons why assuming

TABLE 9. J_λ' VALUES AT 30°N LATITUDE[a,b]

Wavelength Range, nm	Solstice				Equinox		Season Average			
	Summer		Winter				Spring/Summer		Fall/Winter	
285-295	1.0	16	0		0		1.18	15	0	
295-305	7.40	17	6.80	16	3.98	17	6.24	17	1.78	17
305-315	1.09	19	2.83	18	7.49	18	9.77	18	4.60	18
315-325	2.74	19	1.00	19	2.03	19	2.50	19	1.41	19
325-335	4.98	19	2.11	19	3.82	19	4.58	19	2.79	19
335-345	5.49	19	2.48	19	4.28	19	5.07	19	3.20	19
345-355	6.28	19	3.11	19	4.96	19	5.82	19	3.68	19
355-365	6.49	19	3.10	19	5.13	19	6.01	19	3.92	19
365-375	8.09	19	3.95	19	6.43	19	7.51	19	4.96	19
375-385	7.93	19	3.95	19	6.33	19	7.36	19	4.92	19
385-395	8.12	19	4.12	19	6.51	19	7.55	19	5.09	19
395-405	1.11	20	5.72	19	8.94	19	1.03	20	7.04	19
405-415	1.41	20	7.36	19	1.14	20	1.31	20	8.64	19
415-425	1.47	20	7.80	19	1.19	20	1.37	20	9.37	19
425-435	1.49	20	7.99	19	1.21	20	1.39	20	9.67	19
435-445	1.65	20	8.93	19	1.34	20	1.54	20	1.08	20
445-455	1.90	20	1.04	20	1.55	20	1.77	20	1.25	20
455-465	2.05	20	1.13	20	1.67	20	1.92	20	1.35	20
465-475	2.12	20	1.17	20	1.73	20	1.98	20	1.40	20
475-485	2.15	20	1.19	20	1.75	20	2.01	20	1.42	20
485-495	2.15	20	1.20	20	1.76	20	2.01	20	1.43	20
495-515	4.39	20	2.45	20	3.59	20	4.10	20	2.92	20
515-535	4.44	20	2.49	20	3.63	20	4.15	20	2.96	20
535-555	4.42	20	2.49	20	3.62	20	4.13	20	2.95	20
555-575	4.48	20	2.52	20	3.67	20	4.19	20	2.99	20
575-595	4.64	20	2.62	20	3.80	20	4.34	20	3.11	20
595-635	9.44	20	5.39	20	7.70	20	8.81	20	6.34	20
635-675	9.92	20	5.72	20	8.15	20	9.28	20	6.72	20
675-715	1.00	21	5.85	20	8.27	20	9.39	20	6.84	20
715-755	9.67	20	5.70	20	7.98	20	9.05	20	6.64	20
755-795	9.35	20	5.57	20	7.74	20	8.76	20	6.46	20

[a] Second number in column is the power of ten by which the first number is multiplied.

[b] Units are in photons cm^{-2} day^{-1} as discussed in text.

TABLE 10. J_λ' VALUES AT 50°N LATITUDE[a,b]

Wavelength Range, nm	Solstice		Equinox	Season Average	
	Summer	Winter		Spring/Summer	Fall/Winter
285-295	0	0	0	0	0
295-305	5.7 17	6.0 14	1.12 17	3.763 17	2.55 16
305-315	1.005 19	2.981 17	3.945 18	7.724 18	1.398 18
315-325	2.680 19	1.857 18	1.317 19	2.173 19	5.699 18
325-335	5.0 19	5.429 18	2.714 19	4.162 19	1.314 19
335-345	5.577 19	7.118 18	3.163 19	4.700 19	1.597 19
345-355	6.446 19	8.513 18	3.86 19	5.495 19	1.984 19
355-365	6.659 19	9.536 18	3.923 19	5.670 19	2.057 19
365-375	8.341 19	1.248 19	4.985 19	7.130 19	2.648 19
375-385	8.204 19	1.279 19	4.967 19	7.038 19	2.646 19
385-395	8.427 19	1.070 19	5.165 19	7.255 19	2.816 19
395-405	1.157 20	1.951 19	7.161 19	9.987 19	3.949 19
405-415	1.472 20	2.569 19	9.194 19	1.274 20	5.132 19
415-425	1.540 20	2.792 19	9.715 19	1.337 20	5.478 19
425-435	1.564 20	2.915 19	9.938 19	1.361 20	5.652 19
435-445	1.732 20	3.326 19	1.109 20	1.510 20	6.366 19
445-455	1.996 20	3.91 19	1.283 20	1.743 20	7.413 19
455-465	2.159 20	4.30 19	1.392 20	1.886 20	8.087 19
465-475	2.227 20	4.533 19	1.443 20	1.948 20	8.444 19
475-485	2.261 20	4.685 19	1.471 20	1.981 20	8.659 19
485-495	2.268 20	4.769 19	1.483 20	1.983 20	8.758 19
495-515	4.629 20	9.789 19	3.026 20	4.060 20	1.791 20
515-535	4.682 20	1.001 20	3.069 20	4.109 20	1.823 20
535-555	4.664 20	1.002 20	3.062 20	4.095 20	1.822 20
555-575	4.732 20	1.014 20	3.104 20	4.153 20	1.845 20
575-595	4.903 20	1.063 20	3.228 20	4.308 20	1.926 20
595-635	9.935 20	2.227 20	6.631 20	8.749 20	3.983 20
635-675	1.048 21	2.463 20	7.015 20	9.253 20	3.428 20
675-715	1.061 21	2.610 20	7.165 20	9.40 20	4.431 20
715-755	1.023 21	2.644 20	6.977 20	9.089 20	4.370 20
755-795	9.902 20	2.648 20	6.809 20	8.821 20	4.311 20

[a]Second number in column is the power of ten by which the first number is multiplied.

[b]Units are in photons cm^{-2} day^{-1} as discussed in text.

TABLE 11. EXAMPLES OF HAND COMPUTATION OF PHOTOCHEMICAL RATE CONSTANTS[c,d]

	Avg. Cross-Section (σ_λ)	J'_λ Value	$\sigma_\lambda J'_\lambda$	$\Sigma\sigma_\lambda J_\lambda'$, d^{-1}
— Benzaldehyde[a] Day Rates at 30°N on Summer Solstice —				
285-295	7.10 -20	1.0 16	7.10 -4	7.10 -4
295-305	3.33 -20	7.4 17	2.46 -2	2.54 -2
305-315	3.84 -20	1.09 19	4.19 -1	4.44 -1
315-325	4.30 -20	2.74 19	1.18	1.62
325-335	4.22 -20	4.98 19	2.10	3.72
335-345	3.42 -20	5.49 19	1.88	5.60
345-355	2.76 -20	6.28 19	1.73	7.33
355-365	1.32 -20	6.49 19	8.57 -1	8.19
365-375	7.48 -21	8.09 19	6.05 -1	8.80
			$\bar{k}_p$ =	8.80 d^{-1}
— Biacetyl[b] Day Rates at 30°N on Summer Solstice —				
285-295	1.03 -20	1.0 16	1.03 -4	1.03 -4
295-305	4.98 -21	7.4 17	3.69 -3	3.79 -3
305-315	2.04 -21	1.09 19	2.22 -2	2.60 -2
315-325	1.11 -21	2.74 19	3.04 -2	5.64 -2
325-335	9.61 -22	4.98 19	4.79 -2	1.04 -1
335-345	2.19 -21	5.49 19	1.20 -1	2.25 -1
345-355	3.94 -21	6.28 19	2.47 -1	4.72 -1
355-365	6.10 -21	6.49 19	3.96 -1	8.68 -1
365-375	8.68 -21	8.09 19	7.02 -1	1.57
375-385	1.24 -21	7.93 19	9.83 -1	2.55
385-395	1.88 -20	8.12 19	1.53	4.08
395-415	2.37 -20	1.11 20	2.63	6.71
415-435	2.96 -20	1.41 20	4.17	10.88
			$\bar{k}_p$ =	10.88 d^{-1}

[a]Cross-section data from Berger, 1973.

[b]Cross-section data from Calvert and Pitts, 1966.

[c]Second number in column is the power of ten by which the first number is multiplied.

[d]Units are in photons cm^{-2} day^{-1} as discussed in text.

unity quantum yield will often give high photo rates.

First, the reaction may have a thermodynamic cutoff at a wavelength shorter than the wavelength where all or partial absorption occurs. In an extreme case, the thermodynamic cutoff is at a wavelength beyond the solar region where, if absorption occurs, the energy will be insufficient for any reaction.

Second, many photochemical reactions may be extremely sensitive to quenching. For example, reactions that proceed via a triplet state very often are rapidly quenched by oxygen. The interaction of ground state oxygen, which is a triplet having a low-lying singlet excited state, with excited organic triplet to give the ground state singlet is an electronically allowed transition. Thus the reaction for a compound C with a singlet ground state would be

$$C + h\nu \longrightarrow C^*(\text{singlet}) \longrightarrow C^*(\text{triplet})$$

$$C^*(\text{triplet}) + O_2 \longrightarrow C + O_2(\text{singlet})$$

In some case enhanced intersystem crossing occurs without formation of excited oxygen:

$$C^*(\text{triplet}) + O_2 \longrightarrow C + O_2$$

The effect of oxygen is not only on triplet states. For example, the singlet states of many aromatic hydrocarbons are believed to be readily quenched by oxygen. In these cases the process is referred to as catalyzed intersystem crossing (Turro, 1978).

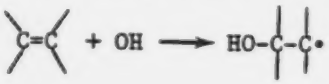
The interaction of excited states with oxygen need not always lead to the ground state. Oxygen may react with excited states which otherwise would not have enough energy to react and which would have returned to their ground state in the absence of oxygen. This has been observed in the photolysis of biacetyl (Porter, 1960; Bouchy and Andre, 1977); yet the number of examples where this has been reported is small.

SECTION 5

PRODUCTS FROM REACTION WITH OH

As discussed above the reactions of OH with organic molecules are composed of three basic types: (1) abstraction of hydrogen-atoms,

(2) addition to carbon-carbon double bonds,



and addition to aromatic rings

The first step in predicting the stable products that result from these reactions in the atmosphere is to determine the relative amounts of these three pathways. For compounds with only one of these pathways open to reaction, the problem is trivial. For compounds having more than one pathway, it is necessary to estimate the rates of each pathway and the relative importance of each. The rate constant for OH attack is estimated by calculating the rate constant for each process. Thus

$$k^{OH}_{total} = k^{OH}(\text{abstraction}) + k^{OH}(\text{C=C addition}) + k^{OH}(\text{ring addition})$$

The actual constants are estimated as discussed in Section 4. The relative importance of three terms is equal to the relative importance of three terms in the above equation. In the examples on page 21, for 1,2-dichloroethane and 1,1-dichloroethane, only H-abstractions are important because they contain no carbon-carbon double bonds on aromatic rings. For the third example, 3-chloro-4-hydroxy -cis-butenoic acid methyl ester, the addition to the C=C double bond is 42/54 or about 78%. The remainder is abstraction at the $-CH_2-$ group (10/54 or 19% and the $-CH_3$ group (1.6/54 or 3.0%) with less than 0.1% involving abstraction of the vinyl hydrogens.

In the fourth example on page 21, there is

86% $-CH_2-$ abstraction and 10% of aromatic ring addition. There is also about 3% abstraction from the CH_3- and about 0.7% abstraction of the aromatic rings hydrogens.

Once the relative importance of each pathway is estimated, the products and their relative importance must be predicted from each pathway.

PRODUCTS RESULTING FROM HYDROGEN ABSTRACTION

Abstraction of hydrogen atoms from most organic compounds results in formation of a free radical with the free valence located on a carbon atom.

$$-\overset{|}{C}-H + OH \longrightarrow -\overset{|}{C}\bullet + HOH \qquad (2)$$

Under atmospheric conditions these carbon radicals react rapidly with oxygen

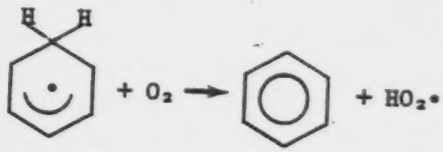
$$-\overset{|}{C}\bullet + O_2 \longrightarrow -\overset{|}{C}O-O\bullet \qquad (3)$$

There are several exceptions to this generalization. One exception is a carbon radical that has an adjacent -OH group. β-H-atom transfer then gives the corresponding carbonyl compound as shown in reaction (4):

$$HO-\overset{|}{C}\bullet + O_2 \longrightarrow HO_2\bullet + \diagdown C{=}O \qquad (4)$$

This alternate pathway may also be important when the O is replaced by N and S; however, we do not have sufficient data to ascertain this fact.

A second type of exception to reaction (3) involves cyclohexadienyl radicals. In this case the reaction is



(5)

This exception is important in the reactions of OH with aromatic compounds and will be considered further in Section 4.

ATMOSPHERIC REACTION OF PEROXY RADICALS

Hydrogen atom abstraction usually leads to formation of the corresponding peroxy radicals as discussed above. The fate of the peroxy radicals is to react with NO even at the extremely low concentrations ($\sim 1 \times 10^9$ molec cm^{-3}, 0.04 ppb). The main reaction is

$$-\overset{|}{C}-OO\bullet + NO \longrightarrow -\overset{|}{C}O\bullet + NO_2 \qquad (6)$$

An alternate reaction may occur in a fraction of the time depending on the organic structure (Darnall, 1976):

$$-\overset{|}{C}OO\bullet + NO \longrightarrow -\overset{|}{C}-ON\overset{O}{\underset{O}{<}} \qquad (7)$$

Thus, the nitrates of all corresponding peroxy radicals should be considered as possible major products (up to 50% of the amount of peroxy radical formed).

The reaction of peroxy radicals with NO_2 is also fast and occurs more readily than with NO because of the generally greater than unity value for the NO_2/NO ratio.

$$ROO\bullet + NO_2 \rightleftharpoons ROONO_2$$

However, to our knowledge, the reaction is totally reversable, and no products result from the interaction. The $ROONO_2$ intermediates can build up to significant concentrations when R equals acyl and aroyl groups, as in the peroxyacyl nitrate (I) and peroxybenzoyl nitrate (II):

$$CH_3\overset{O}{\overset{\|}{C}}O_2NO_2 \qquad\qquad PhC(O)OONO_2$$

I II

Therefore, except for the fraction of peroxy radicals giving nitrate directly from the reaction with NO, the products are determined from the chemistry of the alkoxy radicals.

CHEMISTRY OF ALKOXY RADICALS

Under atmospheric conditions alkoxy radicals undergo both bimolecular and unimoelcular reactions at sufficient rates to be important.

Bimolecular reactions--The important bimolecular reactions of alkoxy radicals are with O_2, NO, and NO_2. The reaction with oxygen is important when α-hydrogens are present in the radical and the β-elimination reactions are relatively slow. The reaction

$$-\overset{H}{\overset{|}{C}}-O\bullet + O_2 \longrightarrow >O + HO_2\bullet \qquad (8)$$

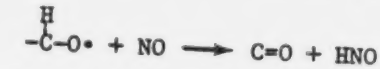
is the major atmospheric reaction for $CH_3O\bullet$ and $CH_3CH_2O\bullet$ and one of the major reaction routes for sec-alkoxy radicals.

The reactions with NO and NO_2 occur with all alkoxy radicals to give nitrite and nitrate, respectively, by the reactions

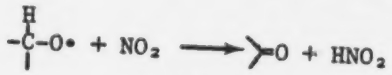
$$RO\bullet + NO \longrightarrow RONO \qquad (9a)$$

$$RO\bullet + NO_2 \longrightarrow RONO_2 \qquad (10a)$$

However, the fate of the alkyl nitrite formed in reaction (92) is to rapidly ($t_{\frac{1}{2}} < 0.5$ hr) photolyze (reforming the alkoxy radical, see Section 7) and thus is unimportant. In cases where the alkoxy radicals have α-hydrogens a small fraction of the time, an alternate reaction occurs:



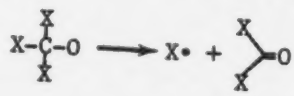
(9b)



(10b)

At the maximum concentrations of NO and NO_2 ($\sim$ 0.1 ppm), reactions (9a) and (10a) are usually unimportant but might be important in special cases depending on the competing reactions. Reactions (9b) and (10b) will always be less important. Because these reactions produce the same products as reaction (8), which will always be competitive, they can be ignored for the purposes of identifying products that might be formed.

Unimolecular reactions—Two types of unimolecular reactions are possible. Generally the most important are the β-elimination reactions, which result in major degradation of the organic structures. The general reaction is



(11)

where X represents various types of groups and will vary within each alkoxy radical in most cases. The rate of reaction is determined not only by the difference in the bond strength of the carbonyl group that is formed over that of the X-C bond as it is broken, but also by the changes in the bond strengths of the other X-C bonds that are not broken. Thus, the rate of eliminating one X is determined by the other Xs that are not broken.

A simple approach to this problem is to assume that each of three X groups in any alkoxy will β-eliminate enough so that the products from all pathways should be considered. In many cases, this approach would predict more products than necessary, but would err on the safe side. We believe some generalizations can be made that can be readily applied to this problem and that will be helpful in minimizing the number of products that are predicted.

Baldwin et al. (1977) have analyzed the available kinetic data on the decompositions of simple alkoxy radicals, and the following generalizations can be made about applying the Arrhenius equation [equation (2)] to these reactions.

$$k_d = Ae^{-E_a/RT} \tag{12}$$

The A factor for the decomposition of primary, secondary, and tertiary alkoxy are $10^{13.6 \pm 0.2}$, $10^{14.3 \pm 0.2}$, and $10^{15.2 \pm 0.2}$ s^{-1}, respectively. In all cases the activation energy is estimated from

$$E_a = 12.8 + 0.71\ \Delta H^\circ_R \text{ (kcal/mol)} \quad \text{if } \Delta H^\circ_R > 0$$

$$= 12.8 \quad \text{if } \Delta H^\circ_R \leq 0$$

Thus from knowledge of the type of alkoxy radical and the heat of reaction (ΔH°_R) for elimination of each of the three groups estimated using techniques discussed by Benson (1976), the rate of reaction for each elimination may be calculated. Table 12 lists the estimated rate constants (k_d) for the elimination of X from the primary radical $X\text{-}CH_2O\bullet$, the secondary radical $X\text{-}CH(CH_3)O\bullet$, and the tertiary radical $X\text{-}C(CH_3)_2O\bullet$. These rate constants are also good approximations for the cases where the methyl groups are replaced with any group where bonding is through carbon.

As an example showing how the rate constants in Table 12 were determined we may consider the reaction

$$CH_3C(O)CH_2O\bullet \longrightarrow CH_3C(O)\bullet + CH_2O$$

The heat of reaction ΔH°_{Rx} is estimated to be 1.3 kcal/mole from the heats of formation of each species. The heat of formation of the initial radical was estimated from the heat of formation of the corresponding alcohol (group additivity) by assuming an O-H bond strength of 104 kcal/mole; the heats of formation of $CH_3C(O)\bullet$ and CH_2O were obtained from standard references (Benson, 1978). Thus using the above equation, $E_a = 13.7$ kcal/mole. Since the reaction involves cleavage of a primary alkoxy radical, $A = 10^{13.2}\ s^{-1}$ and $k = 10^{13.2}\ e^{-13700/RT} = 1.7 \times 10^3\ s^{-1}$ at 300°K. Because of the uncertainties in A and E_a, k has uncertainty of a factor of 10. In cases where the appropriate group values were not available or could not be readily approximated, the heats of reaction were estimated by assuming that the difference in bond strengths of $X\text{-}CH_3$ and $CH_3\text{-}CH_3$ is the same as the difference in heat of reaction for the elimination of X from $X\text{-}CH_2O\bullet$ and CH_3 elimination from $CH_3\text{-}CH_2O\bullet$.

Also included in Table 12 are the apparent first-order rate constants for reaction with O_2 (5×10^{18} molecules cm^{-3}, 160 torr) and NO_2 (2.3×10^{13} molecules cm^{-3}, 0.1 ppm). This latter value corresponds to the maximum concentrations found in a large urban area; in nonurban areas, the value can be lower by a factor of 0.01 to 0.1, in which case the reaction with NO_2 will be that much smaller than the values in Table 12. The rate constants for intramolecular rearrangements are also included and will be discussed below.

Heteroatoms (Y) have various effects on the elimination rates. The effect is most strongly dependent on the change in bond strength of the carbon-heteroatom bond in the elimination process as a second group is eliminated in the reaction

$$X\text{-}\overset{Y}{\underset{}{C}}\text{-}O\bullet \longrightarrow X\bullet + \overset{Y}{\underset{}{}}\!\!>\!C{=}O \qquad (13)$$

The most dramatic effect is when an oxygen atom is in an α-position, for example

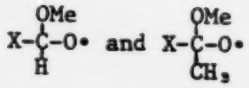
TABLE 12. ESTIMATED RATE CONSTANTS FOR REACTIONS OF PRIMARY, SECONDARY, AND TERTIARY ALKOXY RADICALS

Reaction/Group	Rate Constant,[a] s^{-1}		
	$X-CH_2O\bullet$	$X-C(H)(CH_3)O\bullet$	$X-C(CH_3)_2O\bullet$
β-Elimination			
I-	1.9×10^4	1.5×10^5	7.5×10^5
NO_2-	1.9×10^4	1.5×10^5	7.5×10^5
Br-	1.9×10^4	1.5×10^5	7.5×10^5
$PhCH_2$-	1.9×10^4	1.5×10^5	7.5×10^5
$CH_2=CH-CH_2$-	1.9×10^4	1.5×10^5	7.5×10^5
$CH_3C(O)$-	1.6×10	1.5×10^5	7.5×10^5
$(CH_3)_3C$-	3.0×10^1	1.5×10^5	7.5×10^5
$(CH_3)_2CH$-	8×10^{-1}	2.2×10^4	5.3×10^5
$HOCH_2$-[b]	2×10^{-1}[b]	6.8×10^3	1.6×10^5
CH_3CH_2-	0.2	6.8×10^3	1.6×10^5
CH_3-	7.3×10^{-3}	1.9×10^2	4.5×10^3
CF_3-, $CH_2=CH$-	2.2×10^{-3}	1.0×10	1.4×10^3
H-	4×10^{-8}	7.8×10^{-6}	2.8×10^{-2}
Ph-	0.5×10^{-9}	1.8×10^{-4}	4.6×10^{-3}
F-	1×10^{-13}	6.5×10^{-8}	6.2×10^{-7}
Rx with O_2 and NO_2			
O_2	4.6×10^3	6.4×10^3	0
NO_2(.1 ppm)	4.0×10^1	4.0×10^1	4.0×10^1
δ-H Rearrangements			
primary δ-H	6.0×10^5	6.0×10^5	6.0×10^5
secondary δ-H	3.3×10^6	3.3×10^6	3.3×10^6
tertiary δ-H	3.7×10^7	3.7×10^7	3.7×10^7

[a] See text for method of estimation; rate constant at 300°K uncorrected for pressure effect; at one atmosphere, k/k (at infinite pressure) = 0.003 for 8 atom radical, 0.5 for 11 atom radical, 0.8 for 14 atom radical and 1.0 for larger radicals (Baldwin, 1977).

[b] Limited experimental data suggest this rate constant is effectively 10^3 times faster than indicated or competing reactions are correspondingly slower.

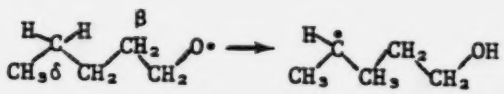
Compared to methyl substituted derivatives (X-), estimates of heat of reaction favor elimination of X and H by several orders of magnitude. In Table 13 we estimated the rate constant for the same substituents for the two cases



The same acceleration effects are expected for all ether groups and -OH. An N-atom in the α position produces approximately the same acceleration in β-elimination as is in -OMe elimination. Thus the data in Table 13 are good estimates for these cases.

The effect of α-halogen atoms depends strongly on the halogen. Fluorine is more like an oxygen substituent whereas iodine is more like a carbon group. Chlorine and bromine are intermediate between fluorine and iodine. Thus, Tables 12 and 13 can be used in many cases to qualitatively determine the important elimination rate constants when α-halogens are present, assuming their effect is intermediate.

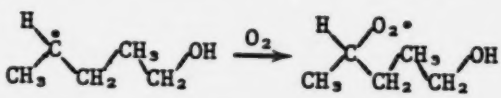
The second type of unimolecular reaction is intramolecular rearrangements which are important for some long chain alkoxy radicals such as



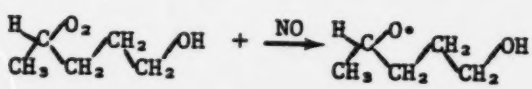
(14)

The rate constants for these reactions have been estimated by Baldwin et al. (1977) for several structures, and these estimates have been included in Tables 12 and 13. The reactions are fast only when there is a hydrogen atom in the δ-position because of the favorable six-membered ring that forms on abstraction. In cases where only five-membered or seven-membered ring rearrangements are possible, the rate is much less and presumably other reactions will dominate.

These six-membered rearrangements result in the formation of disubstituted groups. For the example, in reaction (14) the following reactions will result:



(15)



(16)

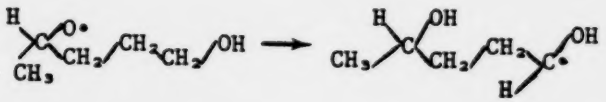
(δ-Rearrangements of $RO_2\cdot$ are too slow to compete with reactions with NO.)

TABLE 13. ESTIMATED RATE CONSTANTS FOR REACTIONS OF METHOXY SUBSTITUTED ALKOXY RADICALS[a]

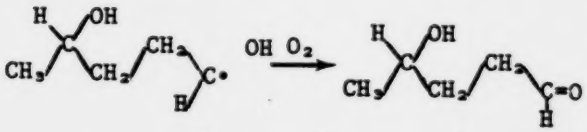
Reaction/Group	Rate Constants, s^{-1}	
	X-CH(OMe)O•	X-C(OMe)(Me)O•
β-Elimination		
I	1.5×10^5	7.5×10^5
NO_2	1.5×10^5	7.5×10^5
Br	1.5×10^5	7.5×10^5
$PhCH_2$-	1.5×10^5	7.5×10^5
CH_2=CH-CH_2-	1.5×10^5	7.5×10^5
$CH_3\overset{O}{\overset{\|}{C}}$-	1.5×10^5	7.5×10^5
$(CH_3)_3C$-	1.5×10^5	7.5×10^5
$(CH_3)_2CH$-	1.5×10^5	7.5×10^5
$HOCH_2$-[b]	1.5×10^5	7.5×10^5
CH_3CH_2-	1.5×10^5	7.5×10^5
CH_3-	1.5×10^5	7.5×10^5
CF_3	1.5×10^5	7.5×10^5
CH_2=CH-	2.0×10^1	2.0×10^3
Ph-H	0.8	6.0×10^2
H-	1.8×10^2	1.5×10^5
F-	9.0×10^{-10}	1.3×10^{-2}
R_x with O_2	6.4×10^3	0
R_x with NO_2 (0.1 ppm)	4.0×10^1	4.0×10^1
δ-H Rearrangement		
Primary δ-H	6.0×10^5	6.0×10^5
Secondary δ-H	3.3×10^6	3.3×10^6
Tertiary δ-H	3.7×10^7	3.7×10^7

[a]See text for method of estimation; rate constant at 300°K uncorrected for pressure effect; at one atmosphere, k/k (maximum pressure) = 0.003 for 8 atom radical, 0.5 for 11 atom radical, 0.8 for 14 atom radical and 1.0 for larger radicals (Baldwin, 1977).

[b]Reaction 8 will dominate.

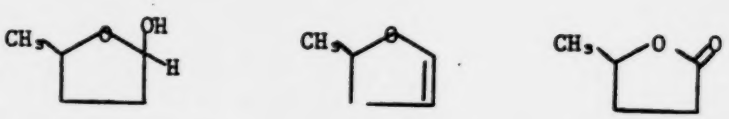


(17)



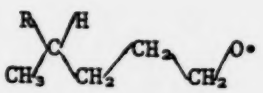
(18)

Other variations can lead to $CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2\overset{O}{\overset{\|}{C}}H$ and $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OH$; condensation reactions of the various products, which would require a heterogeneous surface, can lead to the following structures:

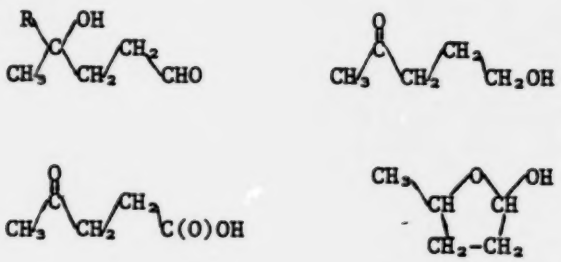


These structures are generalized below in the diagram of the products from intermolecular hydrogen atom transfer:

Starting structure:



Products predicted:



To illustrate how the discussion in this section is applied, we have included Figure 2 which summarizes the reactions of 1,1-dichloroethane in the atmosphere. From this example it is seen that the reaction of one alkoxy radical leads to a second carbon radical, the reactions of which must also be analyzed to determine its fate. The stable products must also be analyzed to determine their lifetime and products of reaction if the total effect of initial compound under consideration is to be determined.

The distribution of products may be estimated from the rate constant data. However because of the uncertainty in the estimated rate constant, it can only be considered qualitative and to point out the relative importance of the possible products. The products in this example greater than 0.01% along with their estimated relative importance are calculated from the relative importance of the pathways as follows:

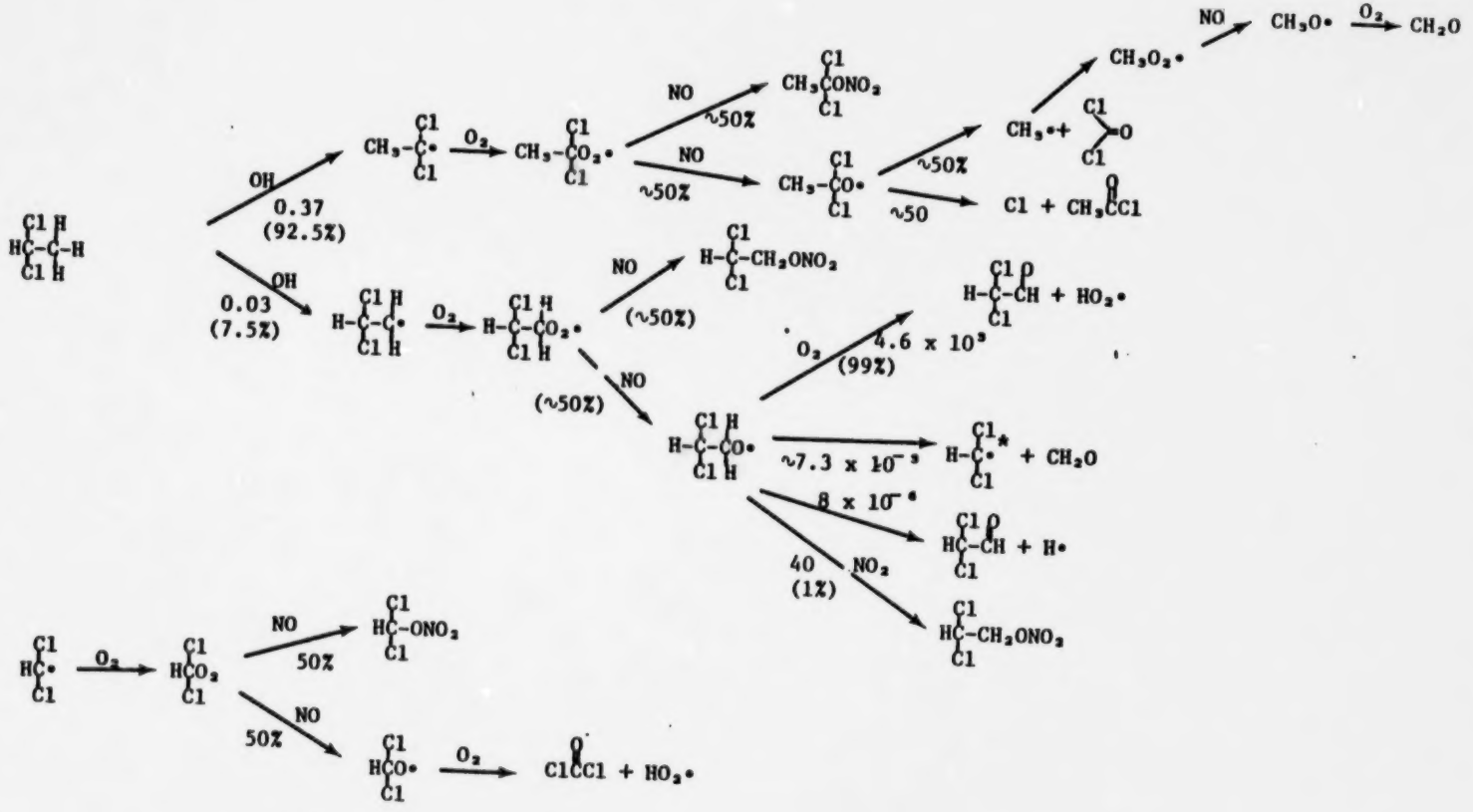


FIGURE 2. PREDICTION OF PRODUCTS FOR 1,1-DICHLOROETHANE

$$CH_3C(Cl_2)ONO_2 = 0.925 \times 0.5 = 0.46$$

$$Cl_2CO = 0.925 \times 0.5 \times 0.5 = 0.23$$

$$CH_2O = 0.925 \times 0.5 \times 0.5 = 0.23$$

$$HCCl_2CH_2ONO_2 = 0.075 \times 0.50 = 0.02$$

$$HCCl_2CHO = 0.075 \times 0.50 \times 0.99 = 0.038$$

$$HCCl_2CH_2ONO_2 = 0.075 \times 0.50 \times 0.01 = 3.8 \times 10^{-4}$$

Thus the first three products should be considered major products (> 10%), and the next two considered minor products (< 10% but > 1%). The last along with $HC(Cl_2)CHO$ and $HC(Cl_2)ONO_2$ would be trace products.

PRODUCTS RESULTING FROM ADDITION OF OH TO C=C DOUBLE BONDS

The OH radical adds rapidly to carbon-carbon double bonds and is usually the major reaction pathway with compounds having this structure. The simplest and best studied example is the reaction of ethene:

$$CH_2{=}CH_2 + OH \longrightarrow HOCH_2CH_2\bullet \qquad (19)$$

The carbon radical formed follows the same chemistry as outlined in the previous section. That is, it reacts first with O_2 and then NO according to the reactions

$$HOCH_2CH_2\bullet + O_2 \longrightarrow HOCH_2CH_2OO\bullet \qquad (20)$$

$$HOCH_2CH_2OO\bullet + NO \longrightarrow HOCH_2CH_2O\bullet + NO_2 \qquad (21)$$

The resulting alkoxy radical should react also as discussed in the previous section. Niki et al. (1978) have shown that the detectable product is formaldehyde, which indicates that β-elimination of $\bullet CH_2OH$ dominates the reaction

$$HOCH_2CH_2O\bullet \longrightarrow HOCH_2\bullet + CH_2O \qquad (22)$$

and then oxygen reacts with the resulting radical as follows:

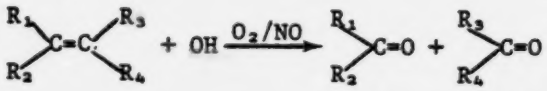
$$HOCH_2\bullet + O_2 \longrightarrow HO_2\bullet + CH_2O \qquad (23)$$

From the information in the previous section, we also expect the following reaction to occur:

$$HOCH_2CH_2O\cdot + O_2 \longrightarrow HOCH_2\overset{O}{\overset{\|}{C}}H + HO_2\cdot \qquad (24)$$

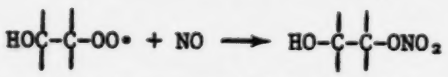
The high yield of formaldehyde rules out appreciable amounts of this reaction. Why the predictive scheme does not anticipate this effect is not clear; the scheme may reflect a unique chemical behavior of α-OH alkoxy radicals or possibly a more general flaw in the procedure when applied to systems containing heteroatoms.

Although the study of the reactions of other olefins under simulated atmospheric conditions are complicated by reactions of ozone, they further support the idea that OH effectively cleaves the carbon-carbon double bond, resulting in two carbonyl-containing molecules as seen for ethene by Niki et al. (1977). Thus, the reaction of olefins and OH is best generalized as follows:



(25)

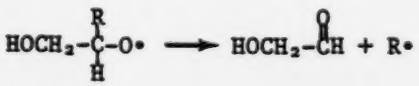
This generalization may suffer from over simplification, and two questions need to be answered. First, if the following reaction of β-hydroperoxy radical, the intermediate formed in reaction (20), ever important?



(26)

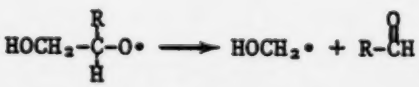
In the limited number of olefins studied, there is no evidence for such a reaction although a search was not specifically made. However, because peroxy radicals from large alkanes (> C_3) have been suggested to undergo this type of reaction a fraction of time, it is not clear why such a reaction should not be important for the olefin reactions where similar intermediates are formed.

A second problem that deserves further study is what controls the cleavage of the β-hydroxy alkoxy radicals in reaction (22). From our discussion in the previous section the reaction,



(27)

should compete if the ΔH_{R_x} is more favorable than the alternate pathway, which leads to C=C cleavage

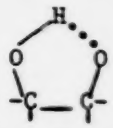


(28)

The effect should be most important when R is a group considerably above $HOCH_2$- in Tables 12 and 13; that is, where R = allyl, benzyl, Br, NO_2, and I. Apparently no one has investigated olefins to see whether this might be the case. In such cases, α-hydroxy aldehydes or ketones would be expected rather

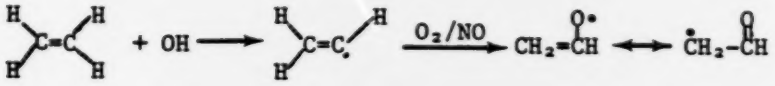
than the two carbonyls that result from C=C cleavage.

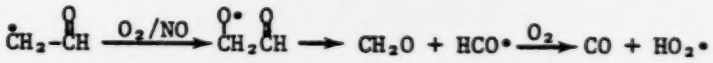
On the other hand, the chemistry of β-hydroxy alkoxy radicals may be unique, possibly due to the intramolecular interaction



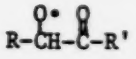
which could favor cleavage to form an HOC• radical [reaction (28)], and this interaction would be independent of competing reactions, either reaction (24) or (27). Further research is needed on this subject if we are going to optimize the reliability of our methods for predicting tropospheric products for complex compounds.

The abstraction of vinyl hydrogen is believed to compete with OH addition. Although the amount of this reaction is expected to be small compared with addition (∿ 0.1%), the products can be sufficiently different in structure that they should be noted. The abstraction route for ethene results in double bond cleavage

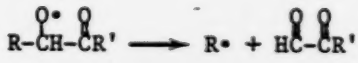




For complex structures, R-CH=CH-R', the following intermediate is obtained:



which can decompose (Section 3)



To illustrate the prediction of products using equation (25), we have summarized in Figure 3 the OH reaction pathway and products for example 3 of the tabulation on page 21 (subsection Hydroxyl Radical Reactions). In this example, addition and cleavage of the carbon-carbon double bond is expected to predominate (∿ 80% of reactions). Hydrogen abstraction reactions will account for the remaining products.

PRODUCTS RESULTING FROM ADDITION TO AROMATIC COMPOUNDS

The OH radical adds at a rapid rate to aromatic rings. For example, the reaction between OH and toluene is believed to give largely ring addition with a small fraction of abstraction from the benzylic methyl group (∿ 15%). The reactions in the atmosphere are believed to be

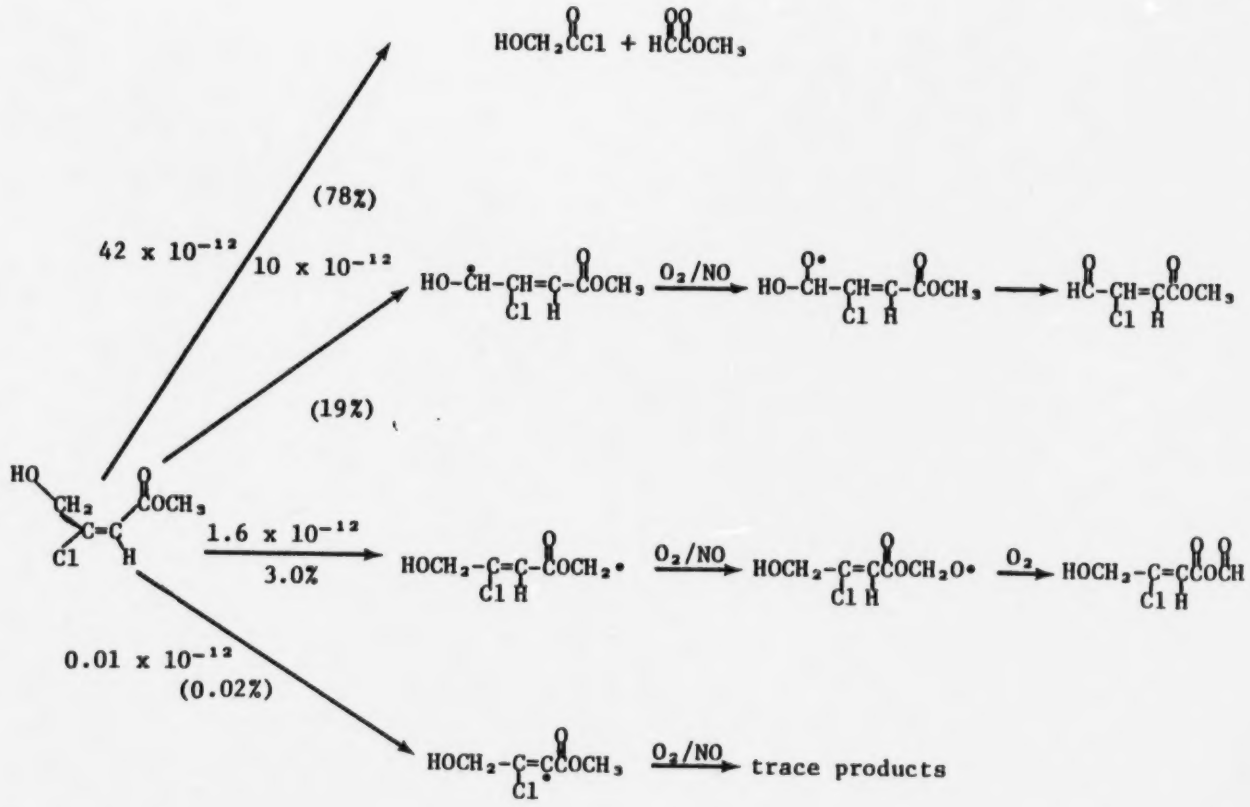
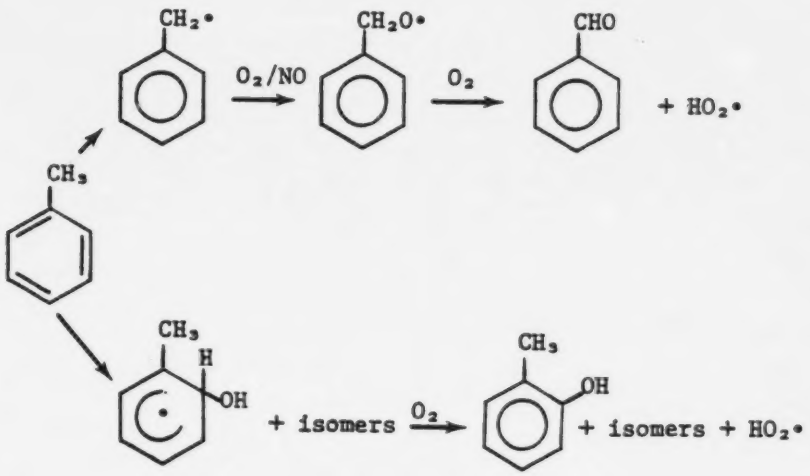
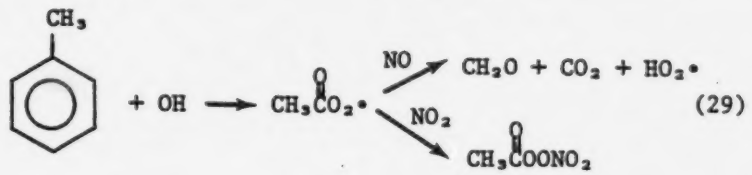


FIGURE 3. PREDICTION OF PRODUCTS FOR 3-CHLORO_4-HYDROXY-CIS-BUTENOIC ACID METHYL ESTER

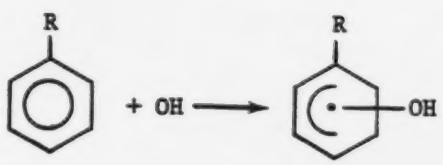


The distribution of cresols are o-: m- : p- = 1.0: 0.06: 0.17; thus 80% of the cresols is the ortho isomer. In smog chamber experiments designed to simulate atmospheric conditions the amounts of cresols suggest alternate routes that involve cleaving the aromatic ring. For example, in the case of toluene, formaldehyde and peroxyacetyl nitrate are formed by an unknown mechanism.

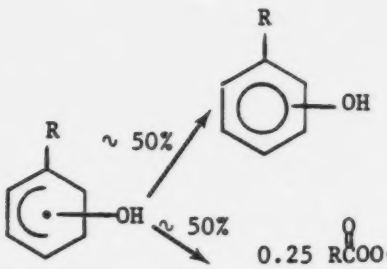


(29)

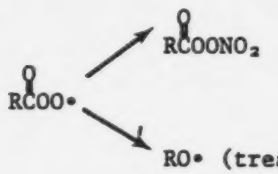
It is not clear at this time whether this alternative involves cresol as an intermediate or if the formation occurs by a route parallel to cresol formation. Ring cleavage is also assumed to form dicarbonyl compounds, such as glyoxal and substituted glyoxals, although they have not been detected. For product estimation, the best generalization appears to be that addition of OH to aromatic leads to phenol formation and ring cleavage in equal amounts with the following breakdown:



(30)



$$0.25\ \mathrm{RC(O)OO\bullet} + .75\ \mathrm{RC(O)CH} + 2\ \mathrm{HC(O)CH} \qquad (31)$$



(32)

The experimentally determined rate constants for addition of OH to aromatic rings indicate that the rate is very sensitive to the type of ring substitution. In Figure 1 we have plotted the rate constants reported by Perry et al. (1977) as addition rate constants versus the summation of para σ_p-constants (Chapman and Shorter, 1972). Because OH is an electrophilic species, a correlation with the electron donating-withdrawing properties of the substrate is a reasonable assumption. Summing of σ-constants for the various substituents oversimplifies the effect of multiple substituents because there is no way to account for the effects of positional isomers. However, as seen in Figure 1, a reasonable correlation of the data covers a factor of 50 in rate constants. The least squares regression line of all data gives

$$\log k_A^{\Sigma X} = 11.578 - 2.12\Sigma\sigma_p \qquad (33)$$

The least squares regression line for only the monosubstituted structures gives

$$\log k_A^{X} = - 11.847 - 4.19\sigma_p$$

The values of k_A determined from these regression lines are expected to be reliable estimates of k_A (± 20%).

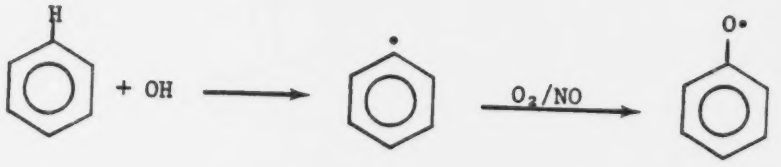
Unfortunately, no data are available for strong electron-withdrawing substituents, except for a limit value for X=-CHO where abstraction of the CHO hydrogen is very fast. From equations (33) and (34), it is possible to estimate the k values of compounds with such substituents, using the list of σ-values in Table 14 taken from Chapman and Shorter (1972).

Competing with addition to aromatics is abstraction of the aromatic hydrogen. This reaction is slow compared to addition but is thought to produce different products. Two types of products are expected: quinone and ring cleavage products. The following are examples of the proposed chemistry for benzene:

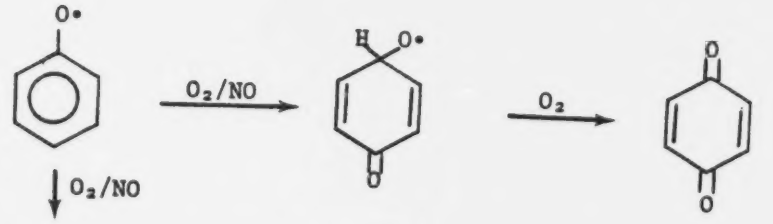
TABLE 14. SELECTED VALUES OF HAMMETT σ_p[a]

Substituent	σ_p	Substituent	σ_p
H	0	NCS	0.38
D	0	N=NPh	0.33
$B(OH)_2$	0.12	N_3	0.15
Me	-0.16	NO_2	0.80
Et	-0.14	PPh_2	0.19
Pr	-0.15	$POPh_2$	0.53
Bu	-0.18	$PO(OEt)_2$	0.60
C≡CH	0.23	OH	-0.36(-0.37)
C≡CPh	0.16	OMe	-0.27(-0.27)
cyclo-C_3H_7	-0.21	OCF_3	0.35
Ph	0.02	OPh	0.32
CH_2Ph	-0.09	OC(O)Me	0.32
CH_2CN	0.18	SH	0.14
CH_2OR	0.03	SMe	0.16
$CH_2SO_2CF_3$	0.31	SCF_3	0.15
CH_2Cl	0.12	S(O)Me	-0.05(0.00)
CF_3	0.55(0.54)	$S(O)_2Me$	0.42
CCl_3	0.46	$S(O)_2CF_3$	0.57(0.49)
CN	0.69	$S(O)_2NH_2$	0.73
CHO	0.43	SO_2F	0.93
COMe	0.44	SF_5	0.91
$C(O)NH_2$	0.38	SeMe	0.60
CO_2H	0.42	$SeCF_3$	0.91
CO_2R	0.43	SC(O)Me	0.68
$SiMe_3$	0.00	F	0.0
NH_2	-0.57	Cl	0.38
NMe_2	-0.60(-0.83)	Br	0.42
NHAc	-0.09	I	0.06(0.06)
NHBz	-0.19	IO_2	0.23(0.23)
$NHC(O)CF_3$	0.12	NMe_3	0.27
N_3	0.78	SMe_2	0.96

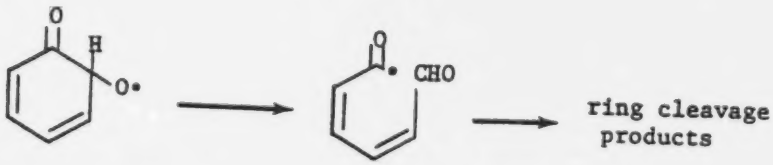
[a]Chapman and Shorter (1972).



(35)



(36)



(37)

The ring cleavage products are expected to be similar to those in reaction (31).

To demonstrate the application of these techniques in Figure 4, we have analyzed compound 4, 3-chloroethylbenzene, from the tabulation on page 21. From equation (33), when $k_A^{OH} = 1.5 \times 10^{-13}$ molec cm^{-3} s^{-1}, we see in Figure 4 that attack at the benzylic $-CH_2-$ group accounts for $\sim$ 93% of the reaction; thus m-chloro benzaldehyde and n-chloroacetophenone are expected to be major products. Ring addition, which is relatively unimportant because of the deactivating effect of Cl, gives $\sim$ 1% of the phenol isomers and similar amounts of products from ring cleavage. Attack at the CH_3 groups also gives m-chlorobenzaldehyde (4%). Abstraction from the ring will also lead to 1% of products from ring cleavage.

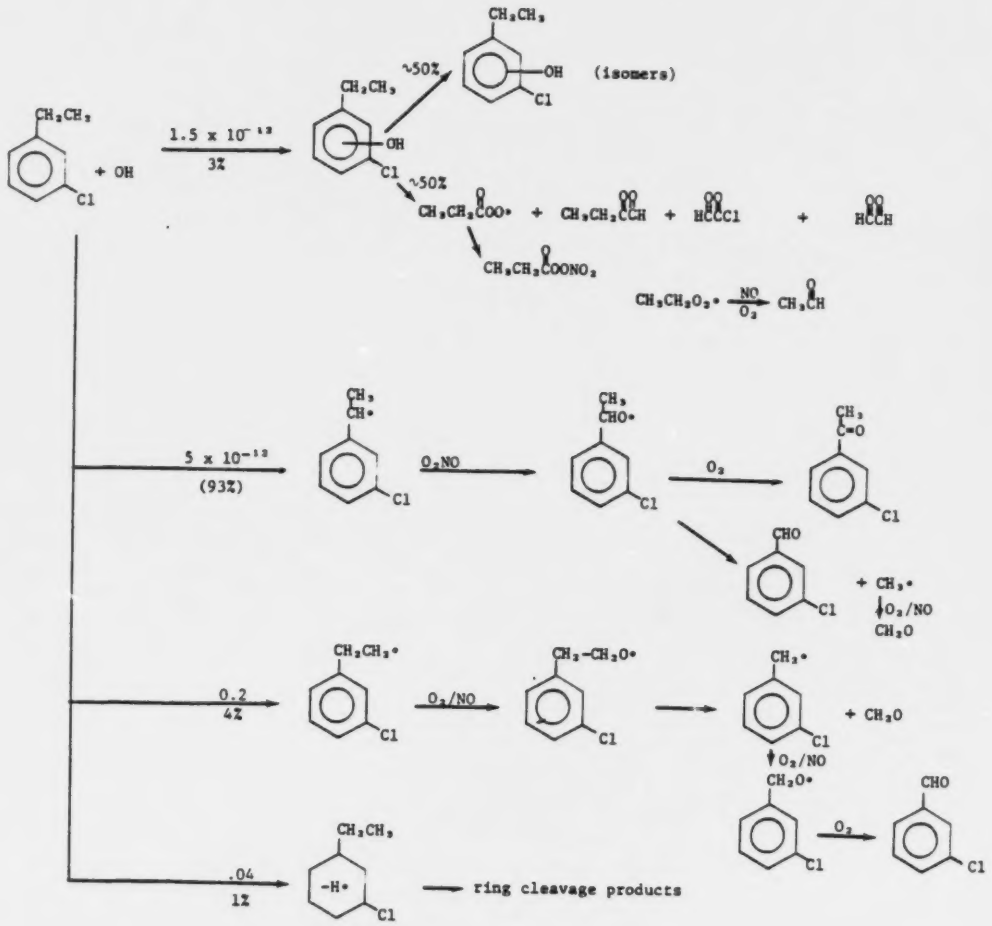
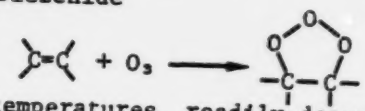


FIGURE 4. PREDICTION OF PRODUCTS FOR 3-CHLOROETHYLBENZENE

SECTION 6

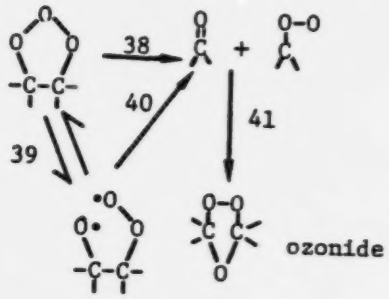
PRODUCTS FROM THE REACTIONS OF OZONE

The most important reactions or organic compounds with ozone in the atmosphere are the reactions of olefins. The reaction is believed to involve the initial formation of molezenide



(37)

which, at atmospheric temperatures, readily decomposes by the following reactions:

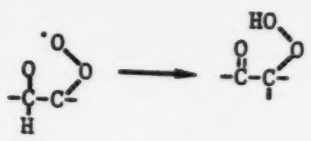


III IV

Reactions (39) and (40) are believed to be the major pathways, but reaction (38) cannot be ruled out. The initially formed products are one mole each of carbonyl compound and the percarbonyl intermediate, referred to as the switterion or methylene peroxy radical; the electronic structure of this latter intermediate appears to be singlet biradical. (Wadt and Goddard, 1975).

Under special conditions the ozonide (IV) has been reported (Niki et al., 1977) but at typical atmospheric concentrations is not expected to form.

O'Neal and Blumstein (1973) have suggested that the diradical intermediate (III) might have a lifetime long enough so that intramolecular reactions, such as the following one, could be important:



(43)

III

However, new data on alkoxy cleavage (Baldwin et al., 1978) suggest that the decomposition by reaction (41) would proceed too fast under environmental conditions for reaction (43) to be important. Experimental results explained by this reaction should be reconsidered to determine if reactions of OH with the alkene can account for the same products.

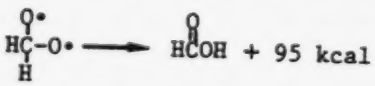
There now appears to be no question as to the intermediary of the percarbonyl intermediates but their chemistry is not well understood. Unimolecular rearrangements of percarbonyl intermediates appear to dominate any bimolecular reactions with NO, NO_2, O_3, or even O_2. The simplest and probably the most rapid reaction is collapse of the biradical to the three membered ring structure, dioxirane:

dioxirane (44)

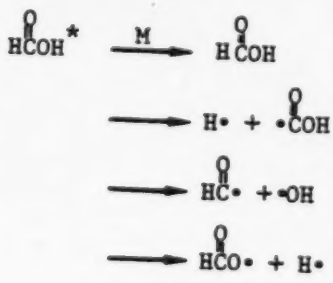
The simplest dioxirane intermediate has been detected in the reaction of ozone and ethene by Martinez et al. (1977), using photoionization mass spectrometry and by Lovas and Svenram (1977), using microwave spectroscopy. However, above -100°C this intermediate decomposes rapidly even at low pressures, which should dramatically stabilize molecules of such low molecular weight; therefore, the intermediate is expected to be extremely labile at atmospheric conditions. The pathway open to the dioxirane structure is cleavage of the extremely weak (∿ 12 kcal/mole) O-O bond to form the dialkoxy radical, dioxymethylene.

(45)

Wadt and Goddard (1977) have suggested that in the simple case, $CH_2(O\bullet)_2$, hydrogen atom migration to form formic acid is the favored reaction:



The overall conversion of the peroxycarbonyl to formic acid is exothermic by at least 140 kcal/mole. Because each step can proceed rapidly relative to collision at one atmosphere, the formic acid can be formed with most of this excess energy. The molecules of hot formic acid have been suggested to deactivate and decompose in several ways (Herron and Huie, 1977; Golden, 1978):



(46)

(47)

(48)

(49)

$\longrightarrow H_2 + CO_2$ (50)

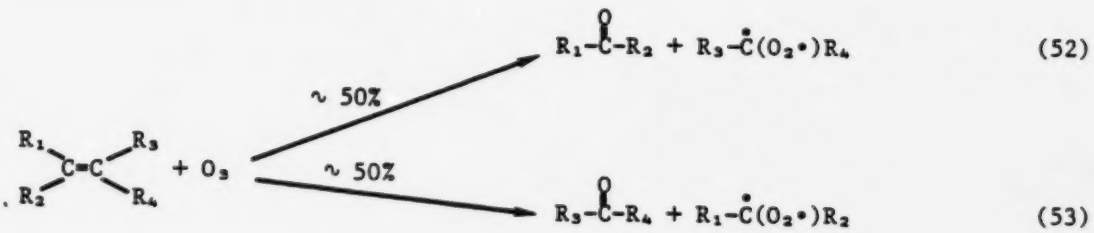
$\longrightarrow HOH + CO$ (51)

Determination of the products of the reaction of $O_3 + CH_2{=}CH_2$ under atmospheric conditions is complicated by the formation of radicals ($HO_2\bullet$ and OH), which react with O_3, $CH_2{=}CH_2$ and the products, especially formaldehyde. Thus, an accurate quantitative description of the products under atmospheric conditions even in this simple case, has not been obtained. Less data are available for more complicated olefins and only a qualitative evaluation can be made. Table 15 reviews some examples of products formed under atmospheric conditions.

TABLE 15. PRODUCTS FROM REACTION OF OZONE AND ALKENES UNDER ATMOSPHERIC CONDITIONS

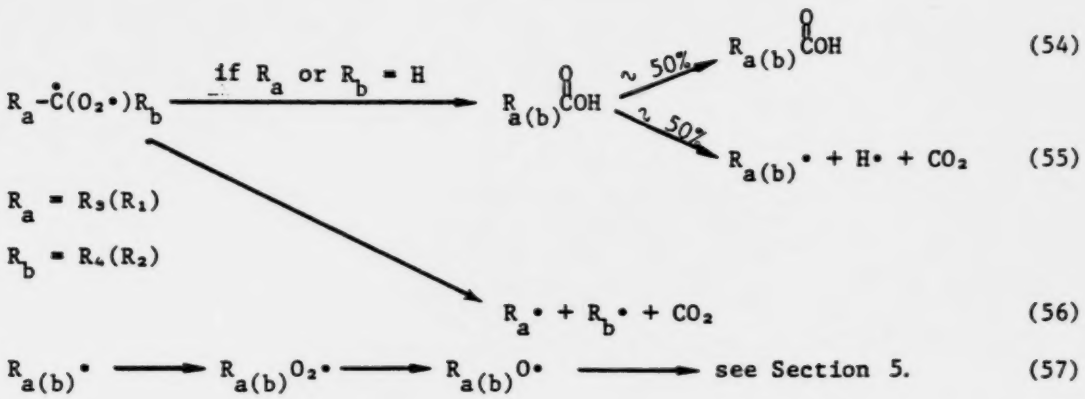
Alkene	Products	Reference
ethene	CH_2O, CO, CO_2, $HCOH$	Scott et al. (1957)
propene	CH_3CH, CH_2O, CO, CO_2, CH_2CO CH_3OH, CH_4	Hanst et al. (1959)
cis-2-butene	CH_3CH, CO_2, CH_4, CH_2O, $HCOH$	Niki et al. (1977)
trans-2-butene	CH_3CH, CO, CH_2O, CH_3OH	Walters et al. (1977)
cis-or trans-1,2-dichloroethene	$HCCl$, HCl, CO, $HCOH$, CCl_2O	Blume et al. (1976)

For predictive purposes the reaction of olefin and ozone may be generalized as follows:



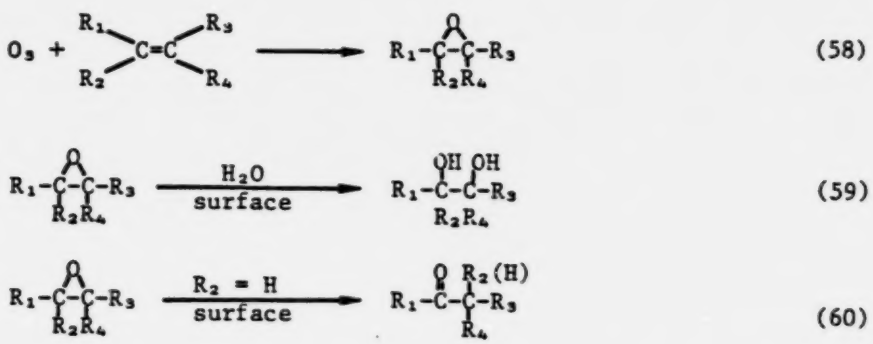
$R_1{-}\overset{O}{\overset{\|}{C}}{-}R_2 + R_3{-}\dot{C}(O_2\bullet)R_4$ (52)

$R_3{-}\overset{O}{\overset{\|}{C}}{-}R_4 + R_1{-}\dot{C}(O_2\bullet)R_2$ (53)



$$R_{a(b)}\cdot \longrightarrow R_{a(b)}O_2\cdot \longrightarrow R_{a(b)}O\cdot \longrightarrow \text{see Section 5.} \qquad (57)$$

In some cases the epoxide of the corresponding olefin has been reported in small yields along with decomposition of the epoxide. Therefore the following reactions may also be important:



This reaction pathway generally does not account for more than 10% of the reaction olefin with ozone. Some workers have reported much higher conversion to these products (Vrbaski and Cvetanovic, 1960), but these results may be caused by the secondary reactions during analysis.

SECTION 7

PHOTOCHEMICAL REACTION PRODUCTS

GENERAL

The predictive model for estimating products of tropospheric photochemical reactions represents a compromise between accuracy, complexity, and general applicability. The model encompasses photochemical reactions that are well-characterized under conditions similar to those in the lower atmosphere as well as some reactions that are less completely understood. Certain types of reactions readily excluded from the scheme are those that cannot occur in the absence of solvent or in the presence of oxygen, reactions that require bimolecular interactions with species other than oxygen, and reactions that require more energy than is available from light in the 290 to 800 nm region of the spectrum. Many important reactions are also excluded from consideration because existing literature data are insufficient to permit reaction mechanisms to be confidently postulated.

These limitations necessarily restrict the number of novel compounds to which the scheme can be applied. However, the compounds for which little literature data exist are frequently those that do not absorb light or are generally known to be photochemically inert in the 290 to 800 nm region. Moreover, the chromophores that can be treated by the present model represent potentially large numbers of new pollutants. Thus, the scheme can be applied to enough molecular types to be of some practical value and also to those types of molecules likely to undergo facile photochemical transformations in the lower atmosphere.

In the following sections the limitations and applicability of the predictive model are described more fully, the general types of reactions that are included in the scheme are discussed, and the specific approach to be used in estimating photochemical products is described in detail.

LIMITATIONS

Although spectral absorption curves cannot be accurately predicted, some general observations can be made regarding chromophores that either do or do not absorb in the 290 to 800 nm spectral region. Clearly, the predictive model only applies to those compounds that absorb strongly in the solar region because reactions with OH or O_3 will generally predominate over photolysis for weak absorbers. Table 16 lists some approximate absorption regions for various molecular types. Because absorption curves typically do not extend to wavelengths as high as 290 nm for aliphatics, nonconjugated olefins, alcohols, ethers, halides (except iodides), amines, disulfides, and carboxylates (acids, esters, and amides), these types of molecules can be disregarded.

TABLE 16. APPROXIMATE ABSORPTION REGIONS FOR ORGANIC MOLECULES

Category	Example	Region nm	Reference
Aliphatics			
hydrocarbons	$n\text{-}C_6H_{10}$	120-170	a
fluorides, chlorides bromides	$CHBr_3$, $CHCl_3$	180-260	a, b
iodides	C_3H_7I	180-320	b
ethers, alcohols	C_2H_5OH, $C_2H_5OC_2H_5$	150-200	a
aldehydes	CH_3CHO	240-340	a
ketones	$C_2H_5C(O)CH_3$	240-320	a, b
acids	$CH_3C(O)O$	200-230	a, b
esters	$CH_3C(O)OCH_3$	200-240	a
amides	$C_2H_5C(O)NHt_2$	180-220	a, b
amines	$(C_2H_5)_3N$	180-240	a, b
azines	$(CH_3)_2C{=}N{-}N{=}C(CH_3)_2$	200-290	b
azo	$CH_3{-}N{=}N{-}CH_3$	200-230, 320-400	a
nitro	CH_3NO_2	200-220, 260-320	a, b
nitroso	$(CH_3)_3CNO$	200-300, 540-740	a
nitrite	$(CH_3)_3CONO$	200-240, 320-400	a, b
nitrate	$C_2H_5ONO_2$	200-300	a
sulfide	$C_2H_5SC_2H_5$	200-220	a, b
disulfide	CH_3SSCH_3	200-240	a, b
Non-conjugated Olefinics and Acetylenes			
hydrocarbons	$(CH_3)_2C{=}C(CH_3)_2$	170-240	a, b
aldehydes	$CH_2{=}CHCHO$	200-250, 290-400	b
ketones	$CH_3CH{=}CH{-}C(O)CH_3$	200-240, 260-330	b
nitro	$CH_3C(NO_2){=}C(CH_3)_2$	180-380	b

[a]Calvert and Pitts (1977).

[b]Perkampus (1971).

On the other hand, aldehydes, ketones and functional groups that feature a double bond to nitrogen (such as nitro and azo compounds, nitrites and nitrates) do absorb in the solar region and must be considered. Note that the table lists only aliphatic and nonconjugated olefins. Compounds that feature extended π systems (such as aromatics, conjugated olefins, and unsaturated heterocycles) normally absorb in the 290 to 800 nm region; these types of molecules (with and without substituent groups) are not excluded on the basis of molecular spectra.

A significant amount of data pertains to the photochemistry of functional groups that do not absorb in the solar region. This data has necessarily been obtained using wavelengths < 290 nm and is not directly relevant to the present case. A question that arises is how to treat those functional groups that normally do not absorb in the solar region but that can absorb when incorporated adjacent to or into a π system. Is the photochemistry of an aliphatic carboxylic acid ester the same as that of an aromatic ester? In some instances, the energetics of the processes will prohibit photochemical reactions with wavelengths > 290 nm, but reasonable mechanisms cannot be excluded. To extend the applicability of the model to as many molecular types as possible, we include in the model certain photochemical reactions that have been studied using only wavelengths < 290 nm. In these instances, the estimated products are classified as possible rather than probable for cases where the photochemistry has been investigated under more relevant conditions.

Because we are required to consider the photochemical reactions that occur under tropospheric conditions, the processes that can be treated by the present scheme are limited. Certainly it is unlikely that photosolvolysis, photoionization, or electron-transfer reactions will occur in the gas phase. Similarly, concentrations of reactive atmospheric species (except oxygen) are low, and bimolecular photochemical reactions such as intermolecular atom abstractions, photoadditions, and photosensitized reactions, are improbable. The effect of oxygen on photofragmentation reactions will be large because the carbon radical fragments from the photolytic reactions will be scavenged by oxygen to form peroxy radicals. This is an important consideration since products derived from peroxy radicals are predictable, using the approach given in Section 5.

Another limiting factor is the energy available in solar radiation. The lower wavelength limit of 290 nm represents a maximum of 98.6 kcal/mole, and any reaction with an activation energy greater than this amount cannot proceed under tropospheric conditions. Table 17 (Benson, 1976) lists bond dissociation energies for some typical organic molecules. These values can be used to determine whether or not a photofragmentation reaction can proceed using solar radiation. For example, most C-F bond homolyses require > 105 kcal/mole and could not occur with 290 nm irradiation. Similarly, cleavage of bonds to substituents (other than halogens) on aromatic rings is unlikely. When considering the photochemistry of aromatics then, we should include reaction pathways other than scission of bonds involving aromatic carbons.

The problem of multiple reaction pathways must also be addressed. As will be seen in the following section, several photochemical reaction mechanisms can be postulated for some chromophores. Although the relative importance of various pathways can be assessed for specific cases, such assessment is not

TABLE 17. BOND-DISSOCIATION ENERGIES FOR SOME ORGANIC MOLECULES $R^{'} - R^{''}$ [a]

	(52.1) H	(19.8) F	(28.9) Cl	(26.7) Br	(25.5) I	(9.5) OH	(46±1) NH_2	(4±1) OCH_3	(34±1) CH_3	(26±1) C_2H_5	(18±1) i-C_3H_7	(8.0±1) t-Bu	(78.5±1) C_6H_5
(34±1)[b]CH_3	104	109	83.5	70	56	91.5	85	82	88	85	84	81	100
(26±1)C_2H_5	98	108	81.5	68	53.5	91.5	84	82	85	82	80	78	97
(21±1)n-C_3H_7	98	108	81.5	68	53.5	91.5	84[c]	82	85	82	80	78	97
(18±1)i-C_3H_7	94.5	105	81	68	53	92	84	82	84	80	77.5	74	95
(8.0±1)t-Bu	92	—	80	64	51	92	84	81	81	78	74	70	92
(78.5±1)C_6H_5	110.5	125	—	78	64	112	105	100	100	97	95	92	116
(45±1)$C_6H_5CH_2$	85	—	—	—	40	77	—	70	72	69	67.5	65	77
(40±1)allyl	87	—	—	—	43.5[c]	80	—	(68)[c]	74.5	71.5	69.5	66	78
(−5)CH_3CO	87	118	82.5	—	51.6	108	101	97	81	78	80	—	95
(−4.5±1)CH_3CH_2O	104	—	—	—	—	43	—	38	81	81	82	82	99
(−1.5)$CH_3CH_2O_2$	90	—	—	—	—	(28)[c]	—	21	72	72	(71)	(69)	91
(67.5±2)CH_2=CH	108	—	91	—	60	—	—	95	99	96	94	92	112

[a] All values are in kcal/mole.
[b] Values in parentheses near radicals and atom are ΔH°_{300}.
[c] Values in parentheses are estimates by the author.

generally possible because of the dependence of product distributions on reaction conditions, such as wavelength, reactant concentration, and solvent versus gas phase. Also, from an environmental standpoint, it is better to predict too many products because products featuring high biological activity (for example, carcinogenicity, and phototoxicity) can have important ecological ramifications if formed even in trace amounts. Given these considerations, no provision has been made for estimating product ratios, and multiple reaction mechanisms must be considered to be equally probable.

As a final note on limitations, we should consider the accuracy and reliability of the model. Many of the reactions described here have been studied in solution, in the absence of oxygen, or using wavelengths < 290 nm; in many cases the assumption that demonstrated reaction mechanisms would be operative in the atmosphere represents an extrapolation of the facts. Also there is no guarantee that an individual photochemical reaction has not been inadvertently excluded from the model. The user should bear these points in mind when assessing the reliability of the method. Only the most straightforward transformations should be regarded as highly probable. Other reactions and mechanisms should be regarded as indicative rather than conclusive. The purpose of the model is not to provide absolute judgements about photochemical reactions but rather to identify and recommend for further study those new compounds that could have a potentially adverse effect on the environment.

PHOTOCHEMICAL REACTIONS

Carbonyl Compounds

Photochemical reactions of aldehydes and ketones are well-characterized and many pertinent examples are known (Calvert and Pitts, 1966; Coyle and Carless, 1972; Turro, 1978). To predict products of photolysis of carbonyl compounds, we need to identify structural features that either permit or disallow one or more of the various reaction mechanisms that can occur.

The first important photochemical reaction to consider is photofragementation [reactions (61a) and (61b)] to produce free radicals.

$$R_1C(O)R_2 \longrightarrow R_\phi C(O)\bullet + R_2\bullet \qquad (61a)$$

$$\xrightarrow{\text{or}} R_2C(O)\bullet + R_1\bullet \qquad (61b)$$

Note that generally cleavage can occur either of two ways to produce different radical fragments. For simple noncyclic aliphatic ketones, both types of cleavage frequently occur and production of all four radical fragments must be considered. In the special case of aromatic ketones, cleavage of the aromatic carbonyl bond is unlikely (because of the high bond dissociation energies for aromatic substitutuents, see Table 17), and only one pair of radical fragments [reaction (62a)] need be considered (Robbins and Eastman, 1970; Pitts et al., 1965).

$$ArC(O)R + h\nu \longrightarrow ArC(O)\bullet + R\bullet \qquad (62a)$$

$$\not\longrightarrow Ar\bullet + RC(O)\bullet \qquad (62b)$$

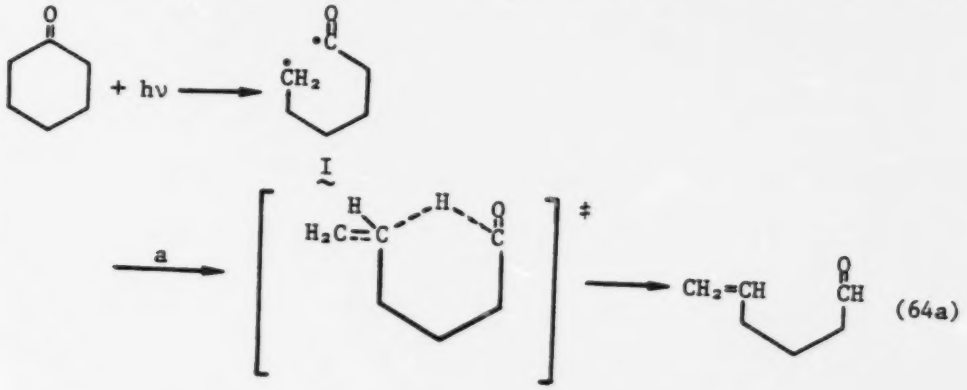
Similarly, for aliphatic aldehydes, reaction (63a) predominates over reaction (63b)

$$R_1C(O)H + h\nu \xrightarrow{a} R_1\bullet + HC(O)\bullet \qquad (63a)$$

$$\xrightarrow{b}\!\!\!\!\!\!\times \quad R_1C(O) + H\bullet \qquad (63b)$$

and direct production of acyl radicals is unimportant (Borkowski and Ausloos, 1962). For aromatic aldehydes process (63b) is favored over (63a) on the basis of the bond dissociation energies involved (Berger et al., 1973), but experimental verification of this is lacking.

In the special case of cyclopentanones and cyclohexanones, photofragmentation yields a diradical, 1, that is prone to intramolecular disproportionation via a 5- or 6-center cyclic transition state, yielding an unsaturated aldehyde [reaction (64a)] or a ketene [reaction (64b)] (Coyle, 1971; Srinivasan, 1963).



(64a)

(64b)

Other cyclic ketones are less likely to undergo intramolecular disproportionation because entropic and enthalpic factors retard the rate for this process to the point where combination of the diradical fragments with molecular oxygen [reaction (52)] is the predominant process.

$$\bullet CH_2(CH_2)_nC(O)\bullet + 2O_2 \longrightarrow \underset{2}{\bullet OOCH_2(CH_2)C(O)OO\bullet} \qquad (65)$$

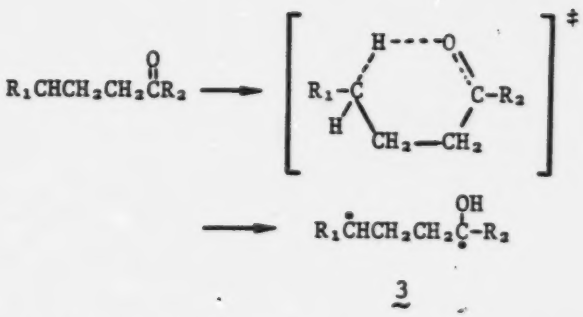
Of course, for acyclic ketones no intramolecular disproportionation is available to the radicals formed by reactions (61a and b), and these species will necessarily be scavenged by molecular oxygen to form peroxy radicals [reaction (66)].

$$R_1C(O)\bullet + R_2C(O)\bullet + R_1' + R_2\bullet + 4O_2 \longrightarrow$$

$$R_1C(O)OO\bullet + R_2C(O)OO\bullet + R_1OO\bullet + R_2OO\bullet \qquad (66)$$

Except for the cyclopentanones and cylcohexanones, photofragmentation of aliphatic ketones will lead to formation of peroxy radicals. The ultimate atmospheric products to be derived from the peroxy radicals will be those predicted by the model described in Section 5 above. Thus, to predict the atmospheric products of the photofragmentation reactions it is necessary to identify only the possible species $R_iOO\bullet$ and $R_jC(O)OO\bullet$ and then refer to the scheme in Section 5 to analyze estimated products. The scheme in Section 5 cannot precisely accommodate reactions of diperoxy radicals, such as 2, and for this reason, products of photofragmentation of cyclic ketones, other than cyclohexanones and cyclopentanones, cannot be estimated beyond the generalization that multifunctional oxygenated species will probably be formed.

An important, and distinctive pathway is available to acyclic aldehydes and ketones that feature a hydrogen atom in an aliphatic carbon γ to the carbonyl group. For these types (Wagner, 1971) an intramolecular hydrogen atom abstraction via a 6-center cyclic transition state yields a diradical, as in reaction (67).

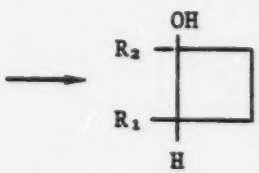


(67)

3

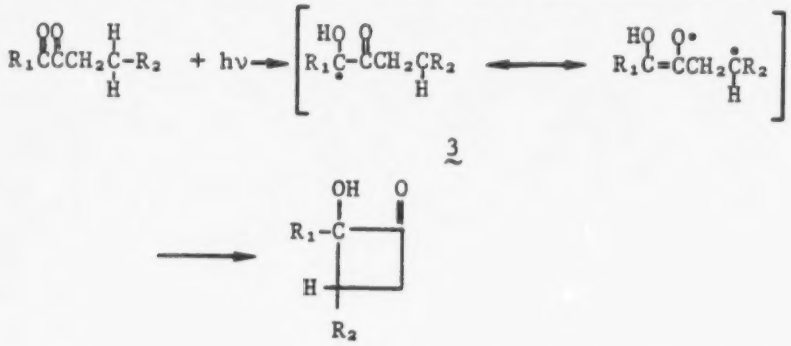
Generally, two reaction pathways are available to 3: (1) elimination to form an olefin and an enol (which typically tautomerizes to the carbonyl compound), and (2) reaction (68a) or cyclization to form a cyclobutanol, as in reaction (68b).

$$3 \longrightarrow R_1CH{=}CH_2 + CH_3C(O)R_2 \text{(from } CH_2{=}\overset{OH}{\overset{|}{C}}R_2) \qquad (68a)$$



(68b)

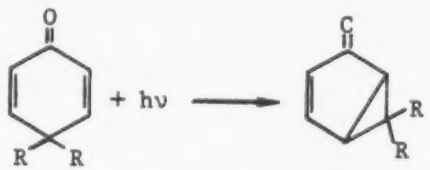
Usually, both reactions (68a) or (68b) cannot occur unless electronic, steric, or ring-strain considerations favor one pathway. Reaction (68b) is especially favorable for α-diketones, (Urry and Trecker, 1962) Urry et al., 1962), presumably because the biradical is resonance stabilized, as in reaction (69)



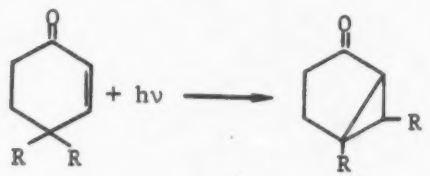
3

(69)

Another aspect of photochemical reactions of carbonyl compounds concerns intramolecular skeletal rearrangements of cyclohexanones and cyclohexadienones, as in reactions (70) and (71) (Kropp, 1967).



(70)



Reactions of carboxylates (acids, anhydrides, esters, and amides) are considerably less certain than those of ketones and aldehydes. Most work has been done with simple aliphatic species that only absorb at short wavelengths. For wavelengths less than 290 nm, sufficient energy is available to produce fragmentation of most bonds in the aliphatic carboxylates. This will not necessarily be the case at higher wavelengths, and to assess the probability of various reactions occuring we must estimate heats of reaction of alternative pathways. Such an estimation can be performed using established methods and available heats for formation of various radical species (Benson, 1976). For example, in the case of acetic acid, the following processes occur at wavelengths < 210 nm (Ausloos and Steacie, 1955):

$$CH_3C(O)OH \longrightarrow CH_3\bullet + \bullet C(O)OH \qquad (72a)$$

$$\longrightarrow CH_3C(O)\bullet + OH \qquad (72b)$$

$$\longrightarrow CH_3C(O)O\bullet + H \qquad (72c)$$

To determine the likelihood of reactions (72a) through (72c) occurring with wavelengths > 290 nm (< 98.6 kcal/mole), we need to calculate heats of reaction for each process. Only those processes with ΔH_R < 98.6 can occur. Using the available data, we estimate the heats of reaction for reactions (72a), (72b), and (72c) to be +88, +109, and +108 kcal/mole, respectively. Thus, only reaction (72a) is likely to occur. For esters, exemplified by $CH_3C(O)OCH_3$, the possible processes are reactions (73a) through (73b).

$$CH_3C(O)OCH_3 \longrightarrow CH_3\bullet + \bullet C(O)OCH_3 \qquad (73a)$$

$$\longrightarrow CH_3C(O)\bullet + \bullet OCH_3 \qquad (73b)$$

$$\longrightarrow CH_3C(O)O\bullet + CH_3\bullet \qquad (73c)$$

The estimated heats of reaction are +82, +85, and +96 kcal/mole, for reactions (73a), (73b), and (73c), and all must be considered possible. Anhydrides, exemplified by $CH_3C(O)OC(O)CH_3$, primarily undergo dissociation as in reaction (74) (Ausloos, 1956):

$$CH_3C(O)OC(O)CH_3 \longrightarrow CH_3C(O)O\bullet + CH_3C(O)\bullet \qquad (74)$$

The estimated heat of reaction (74) is +72 kcal/mole; therefore proceeds the reaction at wavelengths > 290 nm. For amides, such as $CH_3C(O)NH_2$, reaction (75) is dominant at lower wavelengths (Booth and Norrish, 1952).

$$CH_3C(O)NH_2 \longrightarrow CH_3\bullet + \bullet C(O)NH_2 \qquad (75)$$

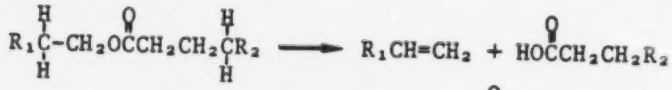
Because the estimated heat of this reaction is +83 kcal/mole, it is expected to occur at longer wavelengths. If aromatic moieties are present in the carboxylates, it is unlikely that photofragmentation will produce phenyl (or substituted phenyl) radicals at longer wavelengths because of the high bond strengths of phenyl-carbonyl bonds.

Possible photofragmentation reactions of carboxylates that absorb at wavelengths > 290 are summarized in the next section. As before, carbon radical fragments will be scavenged by molecular oxygen to produce peroxy radicals, which will give products according to the scheme presented in section 5.

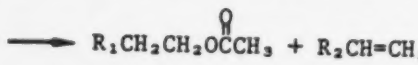
A final category of reactions involving carboxylates is the intramolecular hydrogen atom abstraction and elimination analogous to reactions (67) and (68a) for aldehydes and ketones. For amides with an aliphatic hydrogen γ to the carbonyl, olefins and a shorter chain amide (from the enol tautomer) are produced, as in reaction (76) (Booth and Norrish, 1952).

$$H_2NC(=O)CH_2CH_2\underset{H}{\overset{H}{C}}R \longrightarrow H_2NC(=O)CH_3[H_2NC(OH)=CH_2] + RCH=CH_2 \qquad (76)$$

For esters with γ-aliphatic hydrogens in the acid moiety or β-hydrogens in the alcoholic moiety, reactions (77a) and 77b) can occur (Ausloos, 1958).

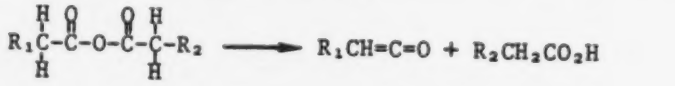


(77a)

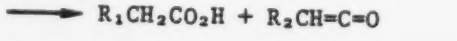


(77b)

The analogous reaction for anhydrides with a β-hydrogen produces an acid and a ketene [reaction (77)] (Ausloos, 1956).



(78a)



(78b)

Analogous reactions for carboxylic acids can be postulated but have not been demonstrated.

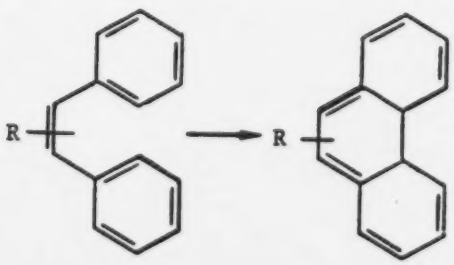
Olefins

Conjugated olefins undergo photofragmentation when irradiated with short-wavelength uv light and at low pressures in the gas phase. In the troposphere with irradiations > 290 nm, such reactions are improbable because of the high bond dissociation energies involved. The atmospheric reactions of conjugated olefins will thus be largely confined to molecular rearrangements such as ring-opening, ring formation sigmatropic rearrangements, and cis-trans, trans-cis isomerizations (Woodward and Hoffman, 1970; Turro, 1978; Coyle, 1974).

Ring closure of conjugated dienes, trienes and cis-stillbenes is represented by reactions (79) through (81).

(79)

(80)



(81)

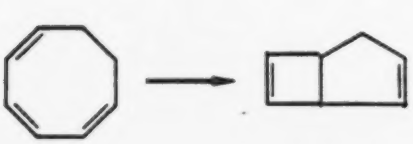
Ring-closure in 7- and 8-membered ring polyenes provides bicyclic olefins, as shown in reactions (82) through (86).

(82)

(83)

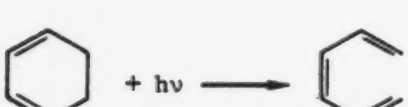
(84)

(85)



(86)

The ring-opening of cyclic olefins is simply the reverse of the corresponding ring-closures, that is



(-72)

Nitrites, Nitrates, Nitro and Nitroso Compounds

This category of compounds is important because they normally feature strong absorbance in the visible range and because they are quite photolabile. The nitro group is particularly effective in causing bathochromic shifts in aromatic compounds.

The primary reaction of aliphatic nitroso compounds is photofragmentation, as in reaction (87).

$$R\text{-}N{=}O + h\nu \longrightarrow R\bullet + NO \qquad (87)$$

As for photofragmentation of carbonyl compounds, the radicals formed initially are rapidly scavenged by molecular oxygen, and the atmospheric products are derived from the corresponding peroxy radicals. For compounds with hydrogen atoms on the carbon β to the nitroso group, an intramolecular elimination [reaction (88)] is also considered possible (Calvert and Pitts, 1966).

$$R_1\overset{H}{\underset{|}{C}}CH_2N{=}O + h\nu \longrightarrow R_1CH{=}CH_2 + HNO \qquad (88)$$

For analogous situation exists for aliphatic nitro compounds, where photofragmentation [reaction (89)] yields carbon radicals and NO_2 (Paszyc, 1974; Glasson, 1975) and cyclic elimination [reaction (90)] produces nitrous acid and an olefin from nitro compounds with hydrogens β to the NO_2 group (Gray et al., 1955).

$$RNO_2 \longrightarrow R\bullet + NO_2 \qquad (89)$$

$$R_1\overset{H}{\underset{|}{C}}HCH_2NO_2 \longrightarrow R_1CH{=}CH_2 + HONO \qquad (90)$$

For aromatic nitro compounds, a different mechanism prevails. In nitrobenzene, photofragmentation [reaction (91)] yields involve N-O homolysis rather than C-N cleavage (Hastings and Matsen, 1948).

$$C_6H_5NO_2 + h\nu \longrightarrow C_6H_5N{=}O + O \qquad (91)$$

This work was performed using wavelengths < 290 nm, but the estimated heat of reaction (+94 kcal/mole) is low enough so that the process should be considered possible at < 304 nm which is just in the solar region. The actual computed photolysis rate constant at 30° N latitude (Section 4) for nitrobenzene using the absorption spectra reported by Calvert and Pitts (1966) and assuming a quantum yield of 1.0 below 305 nm and 0.0 above is 7.6 $days^{-1}$ at the summer solstice and 0.7 day^{-1} at the winter solstice. Thus the lifetime of nitrobenzene in the troposphere will be less than one day except near the winter solstice where it will be slightly greater. This example illustrates how effective a narrow region of the solar spectrum even at the solar cut off can be in causing reaction, if the compound absorbs strongly in this in region such as nitrobenzene does and if the quantum yield is favorable.

Aliphatic nitrites undergo a facile photofragmentation into alkoxy radicals [reaction (92)] (McMillan et al., 1969; Wiebe and Heicklen, 1973).

$$RON{=}O + h\nu \longrightarrow RO\bullet + NO \qquad (92)$$

The fate (and products) of the alkoxy radicals in the atmosphere would be as described in Section 5.

The analogous reaction of aliphatic nitrates is less well understood.

Fragmentation into alkoxy radicals [reaction (93a)] seems likely, but N-O cleavage [reaction (93b)] and cyclic elimination of nitrous acid [reaction (93c)] are also possible (Gray and Style, 1953; Gray and Rogers, 1954; Rebbert, 1963).

$$RCH_2ONO_2 + h\nu \longrightarrow RCH_2O\bullet + NO_2 \quad (93a)$$

$$\longrightarrow RCH_2ONO + O \quad (93b)$$

$$\longrightarrow RCHO + HONO \quad (93c)$$

Halides

Most photochemical studies on organic halides have used wavelengths < 290 nm. Yet, Table 7 shows that carbon halogen bond strengths (except for fluorides) are typically less than the 98.6 kcal/mole maximum energy available in the solar spectrum. This is true even for aromatic and olefinic halides. Therefore, photochemical transformations of organic halides that absorb in the visible region of the spectrum should be considered. The only important photochemical reaction of organic halides is fragmentation into radicals [reaction (94)].

$$R\text{-}X + h\nu \longrightarrow R\bullet + X \quad (94)$$

When more than one type of halogen substituent is present, cleavage involves only the weakest bond (that is, I > Br > Cl > F in order of preferential cleavage). A good example of this type of reaction is photolysis of chloroacetone (Strachen and Blacet, 1955). When 313.0 nm irradiation is used, the principle reaction is C-Cl bond cleavage [reaction 95)]:

$$ClCH_2C(O)CH_3 \longrightarrow Cl\bullet + \bullet CH_2C(O)CH_3 \quad (95)$$

If the halogen substituent is remote from the chromophore, however, the halogen bond is not broken. Thus, for 4-chloro-2-butanone, the reactions (96a) and (96b) proceed to the exclusion of reaction (96c) (Taylor and Blacet, 1956).

$$ClCH_2CH_2C(O)CH_3 + h\nu \longrightarrow ClCH_2CH_2\bullet + \bullet C(O)CH_3 \quad (96a)$$

$$\longrightarrow ClCH_2CH_2C(O)\bullet + \bullet CH_3 \quad (96b)$$

$$\longrightarrow Cl\bullet + \bullet CH_2CH_2C(O)CH_3 \quad (96c)$$

This example is a good illustration of the point that the photolabile group must be in proximity to the chromophore to permit a reaction to proceed.

Aromatic halides (except fluorides) also apparently undergo C-X cleavage to yield halogen atoms or phenyl radical [reaction (97)] (Shoma and Kharasch, 1968; Hee and Sutherland, 1979).

$$Ar\text{-}X \longrightarrow Ar\bullet + X\bullet \quad (97)$$

PROCEDURE

Estimating atmospheric products of photochemical reactions is facilitated

by referring to Table 18. The table summarizes reactions for the various chromophores and functional groups described in the previous section. The general procedure for using the table is as follows. First, identify all chromophores or functional groups in a candidate molecule. Photochemical reactions for each chromophore or functional group listed in the table must be considered. For chromophores or functional groups not listed, no products can be predicted. For a given functional group or chromophore, more than one photochemical reaction may be possible (e.g., for aliphatic ketones, fragmentation and cyclic elimination may be possible). In these cases, all possible reactions are cited. The photochemical products for the reactions to be considered are given in the table. If molecular products are formed directly from the photochemical reaction, they are the atmospheric products. If carbon radicals are formed from the initial photochemical act, combination with molecular oxygen to form peroxy radicals is assumed, and estimation of the atmospheric products is as described in Section 5. When oxy radicals are formed, the atmospheric products are also predicted using the procedure in Section 5.

The photochemical reactions in Table 18 are identified as either probable or possible. The possible reactions are postulated on the basis of work performed on compounds that do not absorb in the solar region.

If a particular functional group is in proximity to or incorporated into a chromophore that absorbs in the 290 to 800 nm, a photochemical reaction involving the functional group may occur. If so, the most probable reaction pathways are those listed in the table. It is important to note that if a functional group is remote from an absorbing chromophore, it is like that photochemical transformation will not occur (see example on the previous page for chloro-substituted ketones).

Care must be taken in using the table when situations involving unusual geometric configurations arise. Steric or ring strain in potential products or ring systems (e.g., aromatic ring substituents located ortho to one another) that place reactive functionalities in close proximity are potentially important effects that cannot be treated in a general fashion. Such occurrences must be considered on a case by case basis, and the user must rely on previous experience in assessing the impact of such effects on product distributions.

As a final work of precaution in applying Table 18, it should be clear that the presence of a structure in the table does not mean the structure photolyzes in the solar spectrum. The table should be only applied to compounds that absorb sufficiently for photolysis to be important. In those reactions which are indicated as "possible," additional chromophores are required to make it possible for these structures to absorb solar light inorder to react.

TABLE 18. PRODUCTS OF PHOTOCHEMICAL REACTIONS

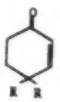
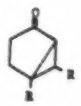
Functional Group	Type	Reaction	Likelihood	Initial Photochemical Products	Atmospheric Products
Ketone: $R_1\overset{O}{\overset{\|}{C}}R_2$	R_1R_2 = alkyl	Fragmentation	Probable	$R_1C(O)\cdot$, $R_2\cdot$, $R_1\cdot$, $R_2C(O)\cdot$	b
	R_1 = alkyl, R_2 = aryl	Fragmentation	Probable	$R_1\cdot$, $R_2C(O)\cdot$	b
	R_1, R_2 = Aryl	Fragmentation	Probable	No reaction	—
	Cyclic: R_1R_2 = $-CH_2(CH_2)_nCH_2-$; n = 2,3	Fragmentation	Probable	$\cdot CH_2(CH_2)_nCH_2C(O)\cdot$	$CH_2{=}CH(CH_2)_{n-1}CO_2H$ $CH_2(CH_2)_{n-1}\overset{O}{\overset{\|}{C}}H$
	n≠2,3	Fragmentation	Probable	$\cdot CH_2(CH_2)_nCH_2C(O)\cdot$	Uncertain[c]
$R_1\overset{H}{C}HCH_2CH_2\overset{O}{\overset{\|}{C}}R_2$	α-Hydrogen on saturated carbon	Cyclic elimination	Probable	$R_1CH{=}CH_2$, $CH_2\overset{O}{\overset{\|}{C}}CH_2$ [enol]	As shown
$R_1\overset{H}{C}CHCH_2\overset{O}{\overset{\|}{C}}R_2$	α-Hydrogen on saturated carbon	α-Hydrogen transfer	Probable	$R_1\overset{\cdot}{C}HCH_2CH_2\overset{\cdot}{C}(OH)R_2$	
	Cyclohexadienone	Rearrangement	Probable		As shown
	Cyclohexenone	Rearrangement	Probable		As shown
Aldehyde: $R_1\overset{O}{\overset{\|}{C}}H$	R_1 = alkyl	Fragmentation	Probable	$R_1\cdot$(0), HC(O)	b
	R_2 = aryl	Fragmentation	Possible	$R_1C(O)$, H·	b
$R_1\overset{H}{C}HCH_2CH_2\overset{O}{\overset{\|}{C}}H$	α-Hydrogen on saturated carbon	Cyclic elimination	Probable	$R_1CH{=}CH_2$, $CH_2\overset{O}{\overset{\|}{C}}H$ [enol]	As shown
Carboxylic acid: $R_1C(O)OH$	R_1 = alkyl	Fragmentation	Possible	$R_1\cdot$, $\cdot C(O)OH$	b
Carboxylic acid ester: $R_1C(O)OR_2$	R_1,R_2 = alkyl	Fragmentation	Possible	$R_1C(O)\cdot$, $R_2O\cdot$, $R_1\cdot$, $\cdot C(O)OR_2$, $R_1C(O)O\cdot$, $R_2\cdot$	b
	R_1 = alkyl, R_2 = aryl	Fragmentation	Possible	$R_1C(O)\cdot$, $R_2O\cdot$, $R_1\cdot$, $\cdot C(O)OR_2$	b
	R_1 = aryl, R_2 = alkyl	Fragmentation	Possible	$R_1C(O)$, R_2O, $R_1C(O)$, $R_2\cdot$	b
	R_1 = aryl, R_2 = aryl	Fragmentation	Possible	$R_1C(O)$, R_2O	b
$R_1\overset{H}{C}HCH_2CH_2\overset{O}{\overset{\|}{C}}OR_2$	γ-Hydrogen on saturated carbon in acid moiety	Cyclic elimination	Possible	$R_1CH{=}CH_2$, $CH_2C(O)OR_2$ [enol]	As shown
$R_1\overset{O}{\overset{\|}{C}}OCH_2\overset{H}{C}HR_2$	β-Hydrogen on saturated carbon in alcohol moiety	Cyclic elimination	Possible	$R_1C(O)OH + CH_2{=}CHR_2$	As shown
Carboxylic acid anhydride: $R_1C(O)OC(O)R_2$	R_1,R_2 = Aryl or alkyl	Fragmentation	Possible	$R_1C(O)$, $R_2C(O)$, $R_2C(O)$, $R_2C(O)O$	b
$R_1\overset{H}{C}HC(O)\overset{O}{\overset{\|}{C}}R_2$	β-Hydrogen on saturated carbon	Cyclic elimination	Possible	$R_1CH{=}C{=}O$, $R_2C(O)OH$	As shown

TABLE 18 (concluded)

Carboxylic acid amide:					
$R_1C(O)NH_2$	R_1 = alkyl	Fragmentation	Possible	$R_1{\cdot}$, $\cdot C(O)NH_2$	b
	R_1 = aryl	Fragmentation	Possible	No reaction	—
$R_1CHCH_2CH_2\overset{O}{\overset{\|}{C}}NH_2$	γ-Hydrogen on saturated carbon	Cyclic elimination	Possible	$R_1CH{=}CH_2$, $CH_2C(O)NH_2$ [enol]	As shown
Olefin:					
$CH_2{=}CH\overset{R}{\overset{\|}{-}}CH{=}CH_2$	Conjugated dienes	Ring closure	Probable	Cyclobutenes	As shown
$CH_2{=}CH{-}\overset{R}{\overset{\|}{C}}H{-}CH{=}CH_2$	Conjugated trienes	Ring closure	Probable	1,3-Cyclohexadienes	As shown
$C_6H_5{-}\overset{R}{\overset{\|}{C}}H{=}CH{-}C_6H_5$	Cis-Stilbenes	Ring closure	Probable	Dihydrophenanthrenes	As shown
$R{-}C_8H_{13}$	1,3-Cyclooctadienes	Ring closure	Probable	Bicyclo[4.2.0]oct-7-ene	As shown
$R{-}C_8H_9$	1,3,5-Cyclooctatrienes	Ring closure	Probable	Bicyclo[4.2.0]octa-2,7-diene	As shown
$R{-}C_8H_9$	Cyclooctatetraenes	Ring closure	Probable	Bicyclo[4.2.0]octa-2,4,7-triene	As shown
$R{-}C_7H_9$	1,3-Cycloheptadiene	Ring closure	Probable	Bicyclo[3.2.0]hept-5-enes	As shown
$R{-}C_7H_7$	1,3,5-Cycloheptatriene	Ring closure	Probable	Bicyclo[3.2.0]hepta-2,5-dienes	As shown
$R{-}C_6H_7$	1,3-Cyclohexadienes	Ring closure	Probable	1,3,5-Hexatrienes	As shown
$R{-}C_4H_5$	Cyclobutenes	Ring closure	Probable	1,3-Butadienes	As shown
Nitroso compounds:					
R-NO	Alkyl	Fragmentation	Probable	$R{\cdot} + NO$	b
$\overset{H}{\overset{\|}{R}}CHCH_2N{=}O$	β-Hydrogen on aliphatic carbon	Cyclic elimination	Possible	$RCH{=}CH_2 + HNO$	As shown
Nitro compounds:					
RNO_2	Alkyl	Fragmentation	Probable	$R{\cdot} + NO_2$	b
	Aryl	Fragmentation	Possible	$RN{=}O + O$	As shown
$\overset{H}{\overset{\|}{R}}CHCH_2NO_2$	β-Hydrogen on aliphatic carbon	Cyclic elimination	Probable	$RCH{=}CH_2 + HONO$	As shown
Nitrites:					
RONO	Alkyl	Fragmentation	Probable	$RO{\cdot} + NO$	b
Nitrates:					
$RONO_2$	Alkyl	Fragmentation	Possible	$RO{\cdot} + NO_2$	b
	Alkyl	Fragmentation	Possible	$RONO + {\cdot}O$	As shown
RCH_2ONO_2	α-Hydrogen on aliphatic carbon	Cyclic elimination	Possible	$RCHO + HONO$	As shown
Halides: (except fluorides)					
R-X	alkyl, aryl	Fragmentation	Possible	$R{\cdot} + X{\cdot}$	b

[a] The word "Probable" under the heading Likelihood indicates that photolysis in the solar has been demostrated, although not necessarily in the presence of oxygen and in the gas phase; the word "Possible" indicates that photolysis has been demonstrated only below 290 nm but the energetics would be favorable for reaction in the solar region if structure is associated with an adjacent chromophore that permitted absorption in the solar region.

[b] Derived from corresponding peroxy radicals; see Section 5.

[c] Multifunctional oxygenated species derived from $\cdot OOCH_2(CH_2)_nCH_2C(O)OO\cdot$.

The first summation accounts for reaction of all reactive hydrogen atoms within the molecule. The term k_{Hi} is the reactivity of the hydrogen atoms from Table 4, taking into account the position and degree of substitution on the adjacent atom by alkyl, vinyl, phenyl, C(O)-, O-, S-, and N- groups. The terms α_{Hi} and β_{Hi} account for the effect of groups in the α-position and β-position on the carbon-hydrogen bond and are also defined in Table 4. These terms are applied for each α and β substituent; thus,

$$\alpha_{H_i} = \Pi\alpha'_{Hi} \cdot \alpha''_{Hi} \cdots \text{ and } \beta_{H_i} = \Pi\beta'_{Hi} \cdot \beta''_{H_i} \cdots$$

The term n_i accounts for the repetition of the i^{th} carbon-hydrogen bond.

The second summation accounts for the reactivity of all carbon-carbon double bonds in the molecule. The term k_E is the intrinsic reactivity of each double bond, taking into account the degree of substitution, whereas α_E accounts for the effect of any halogen substituted directly to the double bond. These terms are defined in Table 5, n_j accounts for the repetition of each unique double bond.

The third summation accounts for addition of OH to aromatic rings in the molecule. The intrinsic reactivity of the ring, k_A, accounts for the degree of alkyl substitution. The α_A accounts for the halogen substituents in the ring. Both k_A and α_A are defined in Table 6. In addition, k_A may be estimated from Figure 1 using valves of σ_p from Table 14.

The sum of the three terms determined k_{OH} (in cm^3 $molec^{-1}$) for the compound. Examples of this calculation are given on page 21.

The lifetime for reaction with OH is

$$\tau_{OH} = 1/k_{OH}[OH]$$

Assuming an average environmental concentration of OH = 10^6 molec/cm^3 (1.7×10^{-15} or 4.1×10^{-8} ppm) the halflife is

$$\tau_{OH} \text{ (seconds)} = 1.0 \times 10^{-6}/k_{OH}$$

Estimation of the Rate Constant for Reaction with Ozone (k_{O_3}) and τ_{O_3}

To estimate the rate constant for the reaction with ozone, the structure of the compound is analyzed for the reactive groups identified in Table 7. Thus, the method involves determining if the compound has a carbon-carbon double; if it does have such a bond, the degree of substitution is determined. Then, from data in Table 7, the rate constant for that specific type of group is determined. If the compound contains an aromatic ring, the degree of substitution is determined and the estimated rate constant is determined also from Table 7. If the molecule contains more than one reactivity group, the molecular reactivity is the sum of the rate constant for each group.

SECTION 8

PREDICTIVE SCHEME

The following is an outline of the predictive procedure.

STEP 1: ESTIMATION OF RATES OF ENVIRONMENTAL PROCESSES

To determine the relative contribution of the various atmospheric chemical processes to the formation of products, we must first determine the lifetimes of the processes. The rate of loss (R_C) of compound C is

$$R_c = -dC/at = \left\{R_{OH}[OH] + k_{O_3}[O_3] + k_p\right\}[C]$$

or expressed in lifetimes, the rate of loss is

$$R_C = \left\{1/\tau_{OH} + 1/\tau_{O_3} + 1/\tau_P\right\}[C]$$

The contribution of each process is proportional to the reciprocal lifetimes. However, $1/t_P$ is only an upper limit, and therefore the importance of the photoreaction can be much less, depending on the quantum yield.

To limit the amount of effort used in estimating products from reactions that will be unimportant relative to the other processes, we suggest the following:

- If $1/\tau_{OH} > 100/\tau_{O_3}$, then products from ozone reactions may be ignored; conversely, if $1/\tau_{O_3} > 100/\tau_{OH}$, then the OH reactions may be ignored. If neither of these inequalities apply, then both processes must be considered.
- If $1/\tau_{OH} > 100/\tau_{O_3} > 100/\tau_p$, then the photo products need not be determined. However, if the inequalities do not apply, the photo products should be determined.

The procedures for estimating $1/\tau$ for each process are given below.

Estimation of the Rate Constant of Reaction with OH (k_{OH}) and τ_{OH}

The rate constant for the reaction with OH may be calculated from the expression

$$k_{OH} = \sum_{i=1}^{i} n_i \alpha_{Hi} \beta_{Hi} k_{Hi} + \sum_{j=1}^{j} n_j \alpha_{Ej} k_{Ej} + \sum_{\ell=1}^{\ell} n \alpha_{A\ell} k_{A\ell}$$

The first summation accounts for reaction of all reactive hydrogen atoms within the molecule. The term k_{Hi} is the reactivity of the hydrogen atoms from Table 4, taking into account the position and degree of substitution on the adjacent atom by alkyl, vinyl, phenyl, C(O)-, O-, S-, and N- groups. The terms α_{Hi} and β_{Hi} account for the effect of groups in the α-position and β-position on the carbon-hydrogen bond and are also defined in Table 4. These terms are applied for each α and β substituent; thus,

$$\alpha_{H_i} = \Pi\alpha'_{Hi}\cdot\alpha''_{Hi}\cdots \text{ and } \beta_{H_i} = \Pi\beta'_{Hi}\cdot\beta''_{H_i}\cdots$$

The term n_i accounts for the repetition of the i^{th} carbon-hydrogen bond.

The second summation accounts for the reactivity of all carbon-carbon double bonds in the molecule. The term k_E is the intrinsic reactivity of each double bond, taking into account the degree of substitution, whereas α_E accounts for the effect of any halogen substituted directly to the double bond. These terms are defined in Table 5, n_j accounts for the repetition of each unique double bond.

The third summation accounts for addition of OH to aromatic rings in the molecule. The intrinsic reactivity of the ring, k_A, accounts for the degree of alkyl substitution. The α_A accounts for the halogen substituents in the ring. Both k_A and α_A are defined in Table 6. In addition, k_A may be estimated from Figure 1 using valves of σ_p from Table 14.

The sum of the three terms determined k_{OH} (in cm^3 $molec^{-1}$) for the compound. Examples of this calculation are given on page 21.

The lifetime for reaction with OH is

$$\tau_{OH} = 1/k_{OH}[OH]$$

Assuming an average environmental concentration of OH = 10^6 molec/cm^3 (1.7×10^{-15} or 4.1×10^{-8} ppm) the halflife is

$$\tau_{OH} \text{ (seconds)} = 1.0 \times 10^{-6}/k_{OH}$$

Estimation of the Rate Constant for Reaction with Ozone (k_{O_3}) and τ_{O_3}

To estimate the rate constant for the reaction with ozone, the structure of the compound is analyzed for the reactive groups identified in Table 7. Thus, the method involves determining if the compound has a carbon-carbon double; if it does have such a bond, the degree of substitution is determined. Then, from data in Table 7, the rate constant for that specific type of group is determined. If the compound contains an aromatic ring, the degree of substitution is determined and the estimated rate constant is determined also from Table 7. If the molecule contains more than one reactivity group, the molecular reactivity is the sum of the rate constant for each group.

The half-life for reaction with O_3 is

$$\tau_{O_3} = 1/k_{O_3}[O_3]$$

Since the average tropospheric ozone concentration is 1×10^{12} molec cm^{-3} (1.7×10^{-9} M or 0.041 ppm), the half-life may be expressed as follows:

$$\tau_{O_3}(\text{seconds}) = 1.0 \times 10^{-12}/k_{O_3}$$

Estimation of the Rate Constant for Photolysis ($\bar{k}_p$) and τ_p

From the absorption spectrum of the compound, the average values of the cross section for the 10 nm intervals used in Tables 8 through 10 are determined and then combined with the corresponding J' values from these tables. The upper limit for the photolysis rate constant ($\bar{k}_p$) is

$$\bar{k}_p = \Sigma \alpha_\lambda J'_\lambda$$

This calculation assumes the photo reaction occurs with quantum yield of unity. The limit for the lifetime is

$$t_p = 1/\bar{k}_p$$

The J'_λ values are in units of day, but for comparison of t_p with the other values they must be converted to second units:

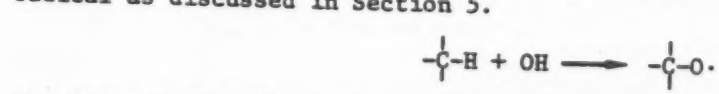
$$\tau_p(\text{seconds}) = 8.64 \times 10^4 \tau_p(\text{days})$$

STEP 2. ESTIMATION OF PRODUCTS FROM OH REACTIONS

All C-H bonds, C=C bonds, and aromatic rings were identified for estimation of the OH rate constant. The products formed from reaction of each of these groups must be determined.

C-H Bond Reactions

Each C-H bond that reacts with OH is assumed to be converted to an alkoxy radical as discussed in Section 5.



The fate of the alkoxy radical determined from Tables 12 and 13 allows one to estimate (1) the rate of β-elimination for each group substituted on the central C atom, (2) the rate of reaction with O_2, (3) the rate of reaction with NO_2, and (4) the rate of δ-H rearrangement if the reaction is possible. The necessary data are listed in the appropriate column in the tables corresponding to the structure of the alkoxy radical.

If the reactions generate additional carbon radicals, then the products from the corresponding alkoxy radicals must also be determined.

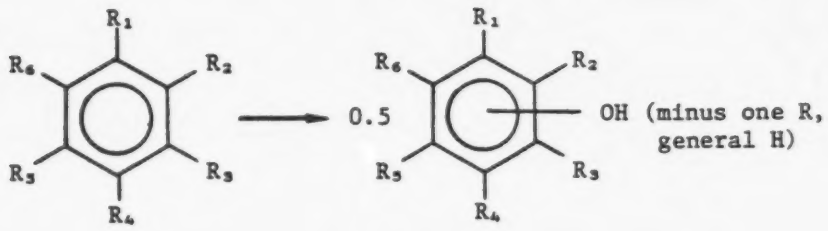
C=C Bond Reactions

For each C=C bond in the molecule, the following general reaction may be assumed:

If one or more of the R groups are hydrogen, it is possible that some hydrogen abstraction may occur, but the amount will be extremely small (0.1%), and this route may be ignored.

Aromatic Ring Reactions

For each aromatic ring the following distribution of products is assumed:



+ 0.5 Ring Cleavage Products

$$\text{Ring Cleavage Products} = \tfrac{1}{2}\, R_1\overset{O}{\overset{\|}{C}}CR_2 + \tfrac{1}{2}\, R_2\overset{O}{\overset{\|}{C}}CR_3 + \tfrac{1}{2}\, R_3\overset{O}{\overset{\|}{C}}CR_4 + \tfrac{1}{2}\, R_4\overset{O}{\overset{\|}{C}}CR_5 + \tfrac{1}{2}\, R_5\overset{O}{\overset{\|}{C}}CR_6 + \tfrac{1}{2}\, R_6\overset{O}{\overset{\|}{C}}CR_1$$

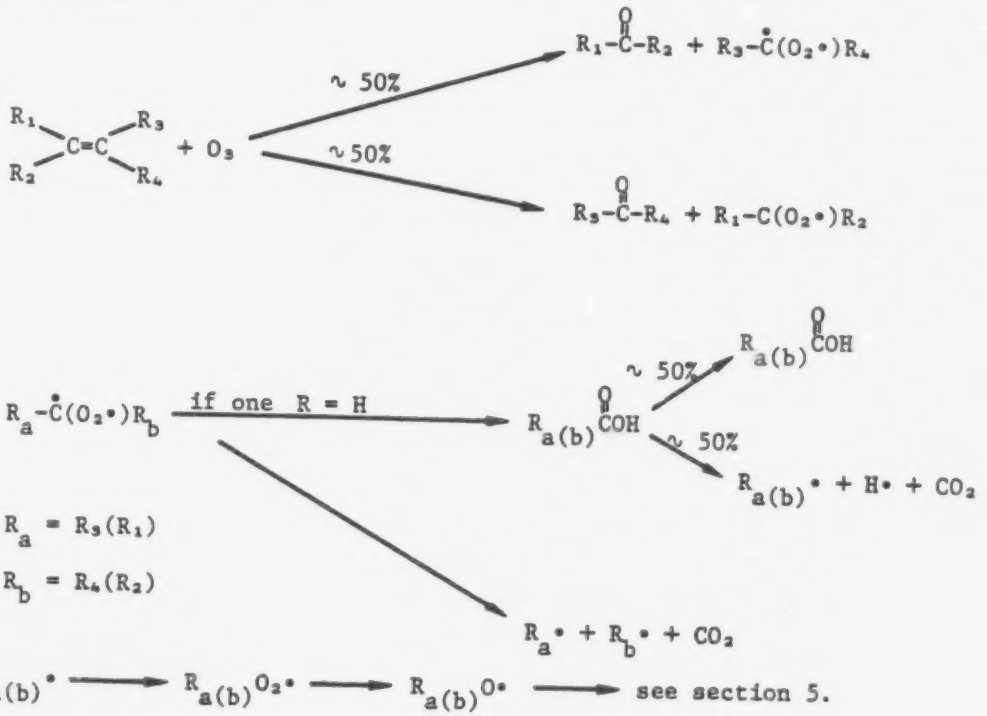
The contribution of hydrogen abstraction from the ring is expected to be small and the products may be ignored.

Relative Amounts of Products

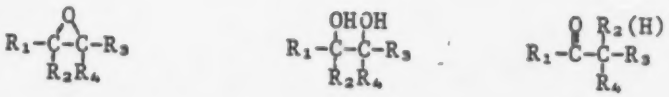
The predominance of each product will depend on the yield in each reaction in which it is formed as well as the relative importance of each process. The relative importance of the various OH reactions may be estimated from the values of k_H, k_E, and k_A which were determined in estimating k_{OH}.

STEP 3: ESTIMATION OF PRODUCTS FROM O_3 REACTIONS

For each carbon-carbon double bond reacting with ozone, the following generalization can be made:



Small amounts (∿ 1%) of the following products may be generally expected:



STEP 4. ESTIMATION OF PRODUCTS FROM PHOTOLYSIS

To estimate the possible products from photolysis, we identified the various chromophores in Table 18. The pathways and products are obtained from the table. For chromophores or functional groups not listed in the table, no products can be predicted.

All the processes are assumed to occur with equal facility in the absence of more detailed data. In cases where carbon radicals or alkoxy radicals are formed, the products of these intermediates are determined as in Step 2.

INDEX

Acids (Carboxylic acids)
OH reactions, 14-21, 30-40
Photolysis reactions, 54, 60, 67

Aldehydes (Alkanols)
OH reactions, 14-21, 30-40
Photolysis reactions, 54, 58, 67

Alkadienes (Dienes, conjugated olefins)
OH reactions, 8, 14-21, 40-42
O_3 reactions, 10, 49-52
Photolysis reactions, 62, 63, 68

Alkanes
OH reactions, 7, 14-21, 30-40
O_3 reactions, 10
Photolysis reactions, 54

Alkanols (Alcohols)
OH reactions, 7, 14-21, 30-40
Photolysis reactions, 54

Alkenes (Olefins)
OH reactions, 8, 14-21, 40-42
O_3 reactions, 10, 11, 49-52
Photolysis reactions, 54, 62, 63, 68

Alkynes (Acetylenes)
OH reactions, 9, 14-21, 40-42
O_3 reactions, 11, 49-52

Amides
OH reactions, 14-21, 30-40
Photolysis reactions, 54, 61, 68

Anhydrides (Carboxylic anhydrides)
OH reactions, 14-21, 30-40
Photolysis reactions, 54, 61, 67

Aromatic Compounds (Aralkanes)
OH reactions, 4, 14-21, 42-48
O_3 reactions, 11, 49-52

Halides
OH reactions, 7, 14-21, 30-40
Photolysis reactions, 54, 65, 68

Cycloalkenes (Cyclic olefins)

OH reactions, 8, 14-21, 40-42
O_3 reactions, 10, 11, 49-52
Photolysis reactions, 54, 62, 63, 68

Esters (Carboxylic esters)
OH reactions, 8, 14-21, 30-40
Photolysis reactions, 54, 61, 67

Ketones (Alkanones)
OH reactions, 7, 14-21, 30-40
Photolysis reactions, 54, 57-60, 67

Nitrates
OH reactions, 14-21, 30-40
Photolysis, 54, 63, 64, 68

Nitrites
OH reactions, 14-21, 30-40
Photolysis reactions, 54, 63, 64, 68

Nitro Compounds
OH reactions, 14-21, 30-40
Photolysis reactions, 54, 63, 64, 68

Nitroso Compounds
OH reactions, 14-21, 30-40
Photolysis reactions, 54, 63, 64, 68

Terpenes
OH reactions, 8, 14-21, 40-42
O_3 reactions, 10, 11, 49-52

REFERENCES

Ausloos, P., and E. W. R. Steacie. 1955. The Vapor Phase Photolysis of Acetic Acid. Can. J. Chem. 33:1530-1535.

Ausloos, P. 1956. The Gas Phase Photolysis of Acetic and Propionic Anhydride. Can. J. Chem. 34:1709-1713.

Ausloos, P. 1958. The Photolysis of Alkyl Esters. Can. J. Chem. 36:383-392.

Baldwin, A. C., J. R. Barker, D. M. Golden, and D. G. Hendry. 1977. Photochemical Estimates and Computer Simulation. J. Phys. Chem. 81:2483-2492.

Benson, S. W. 1976. Thermochemical Kinetics, Second Edition. John Wiley and Sons, Inc., New York.

Berger, M. T., L. Goldblatt, and C. Steel. 1973. Photochemistry of Benzaldehyde. J. Amer. Chem. Soc. 45:1717-1725.

Blume, C. W., I. C. Hisatusune, and J. Heicklen. 1976. Gas-Phase Oznolysis of cis- and trans-Dichloroethylene. Intern. J. Chem. Kinet. 8:235-258.

Booth, G. H., and R. G. W. Norrish. 1952. Photochemical Studies of Some Organic Nitrogen Derivatives. J. Chem. Soc. 188-198.

Borkowski, R. P., and P. Ausloos. 1962. The Vapor Phase Fluorescence and its Relationship to the Photolysis of Propionaldehyde and the Butyraldehydes. J. Amer. Chem. Soc. 84:4044-4048.

Bouchy, M. and Andre, J. C. 1977. Photooxidation of Biacetyl Kinetic Study of Formation of Biacetyl Peroxide and Carbon Dioxide. Molec. Photochem. 8:345-357.

Cadle, R. D. and C. Schadt. 1952. Kinetics of the Gas Phase Reaction of Olefins with Ozone. J. Amer. Chem. Soc. 74:6002-6004.

Cadle, R. D., and Schadt, C. 1953. Kinetics of the Gas Phase Reaction Between Acetylene and Ozone. J. Chem. Phys. 21:163.

Calvert, J. G., and J. N. Pitts, Jr. 1966. Photochemistry. John Wiley and Sons, Inc., New York.

Carter, W. P. L., A. C. Lloyd, J. L. Sprung, and J. N. Pitts, Jr. 1979. Computer Modeling of Smog Chamber Data; Progress in Validation of a Detailed Mechanism for the Photooxidation of Propane and n-Butane in Photochemical Smog. Intern. J. Chem. Kinet. 11:45-101.

Chapman and Shorter. 1972. Advances in Linear Free Energy Relationships. Plenum Press, New York.

Coyle, J. D., 1971. Product Ratios in the Ring-opening Photoreactions of Cycloalkanones. J. Chem. Soc. (B):1736-1740.

Coyle, J. D., and H. A. J. Carless. 1972. Photochemistry of Carbonyl Compounds. Chem. Soc. Rev. 1:329-353.

Coyle, J. D. 1974. The Photochemistry of Olefinic Compounds. Chem. Soc. Rev. 3:329-353.

Darnall, K. R., W. P. L. Carter, H. C. Lloyd, A. M. Winers, and J. N. Pitts Jr. 1976. Importance of RO_2 + NO in Alkyl Nitrate Formation from C_4-C_6 Alkane Photooxidation Under Simulated Atmospheric Conditions. J. Phys. Chem. 80:1948-1950.

Darnall, K. R., R. Atkinson, and J. N. Pitts, Jr. 1978. Rate Constants for the Reaction of OH Radical with Selected Alkanes at 300K. J. Phys. Chem. 82:1581-1584.

Demerjian, K. L., J. A. Kerr, and J. G. Calvert. 1974. The Mechanism of Photochemical Smog Formation. Adv. Environ. Sci. and Tech. 4:1-262.

Glasson, W. A. 1975. Methoxyl Radical Reactions in Atmospheric Chemistry. Environ. Sci. Tech. 9:1048-53.

Golden, D. A. 1978. Organic Free Radicals. Workshop on Chemical Kinetics Data Needs for Modeling the Lower Troposphere. Reston, Virginia.

Gray, J. A., and W. G. Style. 1953. The Photolysis of Ethyl Nitrate. Trans. Faraday Soc. 49:52-57.

Gray, P., A. D. Yoffe, and L. Roselaar. 1955. Thermal Decomposition of the Nitroalkanes. Trans. Faraday Soc. 51:1489-1497.

Gray, P., and G. T. Rogers. 1954. The Explosion and Decomposition of Methyl Nitrate in the Gas Phase. Trans. Faraday Soc. 50:28-36.

Greiner, N. R. 1970. Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI Reactions with Alkanes in the Range of 300-500°K. J. Chem. Phys. 53:1070-1076.

Hampson, R. F., Jr. and D. Garvin. 1978. Reaction Rate and Photochemical Data for Atmospheric Chemistry-1977. National Bureau of Standards Special Publication 513.

Hansen, D. A., R. Atkinson and J. N. Pitts, Jr. 1977. Structural Effects on the Chemiluminescence from the Reaction of Ozone with Selected Organic Compounds. J. Photochem 7:379-404.

Hanst, P. L., E. R. Stephens, W. E. Scott, and R. C. Doerr. 1959. Atmospheric

Ozone-Olefin Reactions. Preprints Petrol. Div., Amer. Chem. Soc. 4:A7-A16.

Hastings, S. H., and F. A. Matsen. 1948. The Photodecomposition of Nitrobenzene. J. Amer. Chem. Soc. 70:3514-3516.

Hee, S.S.Q., and R. G. Sutherland. 1979. Vapor and Liquid Phase Photolysis of the n-Butyl Ester of 2,4-Dichlorophenoxyacetic Acid. Arch. Environ. Contam. Toxicol. 8:247-254.

Heicklen, J. 1966. The Reaction of Ozone with Perfluoroolefins. J. Phys. Chem. 70:477-480.

Hendry, D. G., A. C. Baldwin, J. R. Barker, and D. M. Golden. 1978. Computer Modeling of Simulated Photochemical Smog. EPA-600/3-78-059.

Hendry, D. G. and W. R. Mabey. 1978. Unpublished data.

Hendry et al., D. G. 1979. Test Protocols for Environmental Processes: Air Chemistry (Draft). EPA Contract 68-03-2227.

Herron, J. T., and R. E. Huie. 1977. Stopped-Flow Studies of the Mechanism of Ozone-Alkene Reactions in the Gas Phase Ethylene. J. Amer. Chem. Soc. 99:5430-5435.

Japar, S. M. and H. Niki. 1975. Gas-Phase Reactions of the Nitrate Radical with Olefins. J. Phys. Chem. 79:1629-1632.

Japar, S. M., C. H. Wu, and H. Niki. 1974. Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase. J. Phys. Chem. 78:2318-2320.

Kenley, R. A., J. E. Davenport, and D. G. Hendry. 1978. Hydroxyl Radical Reactions in the Gas Phase. Products and Pathways for the Reaction of OH with Toluene. J. Phys. Chem. 82:1095-1096.

Kropp, P. J. 1967. Organic Photochemistry. O. L. Chapman, Ed. Marcel Dekker, New York.

Leighton, P. A. 1961. Photochemistry of Air Pollution Academic Press, New York.

Lovas, F. J., and R. D. Suenraun. 1977. Identification of Dioxirane in Ozone-Olefin Reactions via Microwave Spectroscopy. Chem. Phys. Letters. 51:453-456.

Martinez, R. I., R. E. Huie, and J. T. Herron. 1977. Mass Spectrometric Detection of Dioxirane and its Decomposition Products from the Reaction of Ozone and Ethylene. Chem. Phys. Letters. 51:457-459.

McMillen, G. R., J. Kumari and D. L. Snyder. 1969. Chemical Reactions in the Urban Atmosphere. C. S. Tuesday, Ed. Elsevier, New York.

Morrissey, R. J., and Schubert, C. C. 1963. The Reactions of Ozone with Propane and Ethane. Combust. Flame 7 263-268.

Nakagawa, T. W., L. J. Andrews, and R. M. Keefer. 1960. The Kinetics of Ozonization of Polyalkylbenzenes. J. Amer. Chem. Soc. 82:269-276.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach. 1977. FTIR Spectroscopic Observation of Propylene Ozonide in the Gas Phase Reaction of Ozone-cis-2-Butene-Formaldehyde. Chem. Phys. Let. 46:327-330.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach. 1978. Mechanism for Hydroxyl Radical Initiated Oxidation of Olefin-Nitric Oxide Mixtures in Parts Per Million Concentrations. J. Phys. Chem. 82:135-138.

O'Neal, H. E. and C. Blumstein. 1973. A New Mechanism for Gas Phase Ozone-Olefin Reactions. Intern. J. Chem. Kinet. 5:397-413.

Paszyc, S. 1974. Photochemistry of Nitro Alkanes. J. Photochem. 2:183-198.

Perkampus, H. H. et al. 1971. UV Atlas of Organic Compounds Vo; I-V. Plenum Press, New York.

Perry, R. A., R. Atkinson, and J. N. Pitts, Jr. 1977. Kinetics and Mechanism of the Gas Phase Reaction of OH Radicals with Aromatic Hydrocarbons Over the Temperature Range 296-473K. J. Phys. Chem. 81:296-304.

Pitts, J. N., Jr., L. D. Hess, E. J. Baum, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, and G. F. Vesley. 1965. Recent Progress in Photobiology. E. J. Bowen, Ed. Blackwells, Oxford.

Pitts, J. N., Jr. and B. J. Finlayson. 1975. Mechanisms of Photochemical Air Pollution. Angew Chem. Intern. Ed. 14:1-74.

Pitts, J. N., Jr. A. M. Winer, K. R. Darnall, A. C. Lloyd, and G. J. Doyle. 1977. Hydrocarbon Reactivity and the Role of Hydrocarbons, Oxides of Nitrogen, and Aged Smog in the Production of Photochemical Oxidants. International Conference on Photochemical Oxidant Pollution and Its Control. Proceedings: Vol. II p. 687-704.

Porter, G. B. 1960. Photooxidation of Biacetyl. J. Chem. Phys. 32:1587-1588.

Rebbert, R. E. 1963. Primary Processes in the Photolysis of Ethyl Nitrate. J. Phys. Chem. 67:1923-1925.

Ripperton, L. A. and H. E. Jeffries. 1972. Formation of Aerosols by Reaction of Ozone with Selected Hydrocarbons. Advances in Chemistry Series. 113:219-231.

Robbins, W. K., and R. H. Eastman. 1970. Photodecarbonylation in Solution. I. Quantum Yields and Quenching Results with Dibenzyl Ketones. J. Amer. Chem. Soc. 92:6076-6077.

Schere, K. L., K. L. Demerijian. 1977. Calculation of Selected Photolytic Rate Constants over a Diurnal Range: A Computer Algorithm. EPA 600/4-77-015.

Schubert, C. C., R. N. Pease. 1956. The Oxidation of Lower Paraffin Hydrocarbons. I. Room Temperature Reaction of Methane, Propane, n-butane, and Isobutane with Ozonized Oxygen. J. Am. Chem. Soc. 78:2044-2048.

Scott, W. E., E. R. Stephens, P. L. Hanst, and R. C. Doerr. 1957. Further Developments in the Chemistry of the Atmosphere. Proc. Amer. Petrol. Inst. 37:171-183.

Shoma, R. K., and N. Kharasch. 1968. The Photolysis of Iodoaromatic Compounds. Angew, Chem. Intern. Ed. Eng. 7:36-44.

Srinivasan, R. 1963. Photochemistry of Cyclic Ketones. Adv. in Photochem. Vol. I. W. A. Noyes, G. S. Hammond, and J. N. Pitts, Eds. Wiley-Intersicence, New York.

Strachan, A. N., and F. E. Blacet. 1955. The Photolysis of Chloroacetone at 3130 Å. J. Amer. Chem. Soc. 77:5234-5257.

Taylor, R. P., and F. E. Blacet. 1956. The Photolysis of Chloroketones. J. Amer. Chem. Soc. 78:706-707.

Turro, N. J. 1978. Modern Molecular Photochemistry. Benjamin/Cummings. Publishing Co., Inc. Menlo Park, CA.

Urry, W. H., and D. J. Trecker. 1962. Photochemical Reactions of 1,2-Diketones. J. Amer. Chem. Soc. 84:118-120.

Urry, W. H., D. J. Trecker, and D. A. Winey. 1962. Photochemistry of 1,2-diketones-1,2-cyclo-decanedione and 2,3-pentanedione. Tet. Lett. 609-613.

Vrbaski, T. and R. J. Cvetanovic. 1960. A Study of the Products of the Reactions of Ozone with Olefins in the Vapor Phase as Determined by Gas-Liquid Chromatography. Can. J. Chem. 38:1063-1069.

Wagner, P. J. 1971. Type II Photoelimination and Photocyclization of Ketones. Accounts Chem. Res. 4:168-177.

Wadt, W. R. and W. A. Goddard III. 1975. The Electronic Structure of the Criegee Intermediate. Ramification for the Mechanism of Ozonolysis. J. Amer. Chem. Soc. 97:3004-3021.

Walter, T. A., J. J. Bufalini, and B. W. Gay, Jr. 1977. Mechanism for Olefin-Ozone Reactions. Env. Sci. Technol. 11:382-386.

Wiebe, H. A., and J. Heicklen. 1973. Photolysis of Methyl Nitrite. J. Amer. Chem. Soc. 95:1-13.

Woodward, R. B., and R. Hoffman. 1970. The Conservation of Orbital Symmetry. Verlay Chemie, Weinheim.

Williamson, D. L. and R. J. Cvetanovic. 1968. Rates of Reactions of Ozone with Chlorinated and Conjugated Olefins. J. Amer. Chem. Soc. 90:4248-4252.